Rotational Isomerism of Disubstituted Benzenes in the Alkylphenyldi-(1-adamantyl)methanol Series

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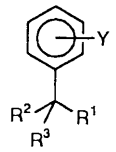
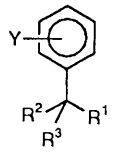
Addition of di(1-adamantyl) ketone to the appropriate tolyllithium compounds gives all five positional and rotational isomers of tolyldi(1-adamantyl)methanol, as evidenced by ^1H and ^{13}C NMR spectroscopy. Synthesis of the *ortho*-substituted derivatives gives essentially the *anti* isomer (*anti/syn* = 11.6), the *meta*-derivatives mainly *syn* (*anti/syn* = 0.77). Thermal equilibration converts *anti,ortho* almost exclusively to *syn,ortho* while the *anti/syn* ratio is virtually unchanged for the *meta* derivatives. The rotation barriers for the *ortho*- and *meta*-derivatives are 39 and 27 kcal mol^{-1}, respectively. The *anti/syn* ratio for the synthesis of the corresponding *meta*-(*tert*-butyl)-substituted alcohols increases with the reaction time. Thermal equilibration indicates that the *anti* isomer is about 0.3 kcal mol^{-1} more stable than the *syn*, due to attractive interactions between the *tert*-butyl group and the adamantyls, whereas the *syn,meta*-tolyl is 0.2 kcal mol^{-1} the more stable. Molecular mechanics calculations slightly exaggerate the stability of the *anti* rotamers. Butyllithium-catalysed rotation of the *meta*-substituted alcohols favours the *anti*-isomers in both cases, much more for Bu^t than for Me. When the *meta*-substituted alcohols are converted to the corresponding methanes by the $(COBr)_2$–Bu_3SnH procedure, rotamerically mixed products are obtained. Again the *syn,meta*-tolyl and the *anti,meta*-(*tert*-butyl)phenyl derivatives are the more stable, by about 0.15 kcal mol^{-1} in both cases. Reaction of *anti,ortho*-tolyldiadamantylmethanol gives a single methane, the *syn* rotamer. The rotation barrier for the *meta*-tolyldiadamantylmethanes is less than 1 kcal mol^{-1} greater than that for the corresponding alcohol. The mechanism of organolithium addition to ketones is discussed.

One of the fundamentals of aromatic chemistry is that there are three isomeric disubstituted benzenes: *ortho*, *meta* and *para*, irrespective of whether the substituents, X and Y, are different or identical. However, if one of the substituents lacks rotational symmetry with respect to the bond to the benzene ring, then it is conceivable that additional *meta* and *ortho* isomers exist, depending on the orientation of the non-symmetrical substituent. Thus, there should be two *meta* and two *ortho* isomers, *syn* and *anti*, where substituent X has been replaced by the group $-CR^1R^2R^3$. The C–R^1 bond, where R^1



syn



anti

is the smallest substituent, will tend to lie close to the plane of the benzene ring and the two isomer types are identified according to the proximity or the remoteness of substituent Y relative to R^1, corresponding to the *syn* and *anti* rotamers, respectively, as shown. As far as the number of disubstituted isomers is concerned it is of no importance whether R^2 and R^3 are the same or different. If, however, R^1, R^2 and R^3 are all different there are potentially five enantiomer pairs of disubstituted benzene derivatives.

A critical point for the practical application of these considerations is that the rotation of the group $-CR^1R^2R^3$ about the C–C_{Ar} bond be slow. Attention has been focused on the alcohols (R^1 = OH); early work,[1,2] mainly on methoxyphenyl(*tert*-butyl)methanols, Ar(Bu^t)R^3COH, showed that the barrier height rose from 8.7 kcal mol^{-1},† when R^3 = H to 21.4 kcal mol^{-1} when R^3 = Bu^t, the coalescence temperature for the latter derivative being 148 °C. Anderson[3] distinguished two conformers of an *o*-tolyl(*tert*-butyl)methanol, its methyl ether and the corresponding methane by low temperature DNMR studies. Lomas isolated *syn* and *anti*-*o*-tolyldi(*tert*-butyl)-methanols and related compounds with very high rotation barriers.[4–6] Crystallographic study on the *syn* isomer[7] and calculations[5] indicate that the preferred structures are, in Anderson's terminology,[3] 'close to parallel', while the 'perpendicular' structures correspond rather to the rotation transition states[6] except when one of the α-substituents is much greater than the other two.[3]

In the present study we have taken advantage of the very high rotation barrier induced by the 1-adamantyl group[6] to isolate the five methyl-substituted derivatives of phenyldi-(1-adamantyl)methanol, $PhAd_2COH$ (Ad = 1-adamantyl). Recently, Olah has reported diastereotopic ^{13}C aromatic resonances in the parent alcohol and *para*-substituted derivatives.‡,[8] Two *meta*-(*tert*-butyl)phenyl and the *para*-(*tert*-butyl)phenyl derivatives are also described. The methanes corresponding to the various alcohols have been synthesised but the *meta*-substituted derivatives, always obtained as mixtures even when isomerically pure starting alcohols are used, have not been completely separated.

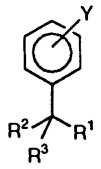
Results

Synthesis.—Alcohols. For the sake of clarity these results will

† 1 cal = 4.184 J.

‡ Olah assumes that the alcohol has C_s symmetry.[8] This can only be correct on a time-averaged basis; calculations[5] and crystal structures[7] on related alcohols show clearly that they are dissymmetric, with the C–O bond about 10° from the plane of the benzene ring, there being a small energy barrier to libration.

be presented as if the rotamers had already been identified, though naturally this identification depends on the NMR analysis related in the following section.



1 $R^2 = R^3 = Bu^t$, Y = H
2 R^2 = Ad, $R^3 = Bu^t$, Y = H
3 $R^2 = R^3$ = Ad, Y = H
4 $R^2 = R^3$ = Ad, Y = *o*-Me
5 $R^2 = R^3$ = Ad, Y = *m*-Me
6 $R^2 = R^3$ = Ad, Y = *p*-Me
7 $R^2 = R^3$ = Ad, Y = *m*-(Bu^t)
8 $R^2 = R^3$ = Ad, Y = *p*-(Bu^t)

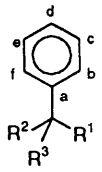
Aryldi(*tert*-alkyl)methanols were prepared by addition of di(*tert*-alkyl) ketone to aryllithium in diethyl ether at room temperature under argon. The syntheses of **1**,[9] **2**, **3**, **6** and **8** are trivial and require no comment. Addition of di(1-adamantyl) ketone to *o*-tolyllithium gave a mixture of the *anti* and *syn* isomers, **4A** and **4S**, in a ratio of 11.6. These were easily separated by column chromatography on alumina. The same reaction with *m*-tolyllithium gave a mixture of two isomers, **5A** and **5S**, in a ratio of 0.77 after column chromatography. Repeated crystallisation from hexane gave the major product, **5S**, almost isomerically pure, while the minor isomer, **5A**, was obtained pure in very small yield from the mother-liquors. *m*-(*tert*-Butyl)phenyllithium with diadamantyl ketone gave an alcohol mixture, **7A** and **7S**, but the rotamer ratio was found to depend on the reaction time, **7A** being progressively formed at the expense of **7S**. It was therefore rather easier to isolate isomerically pure isomers than in the previous case.

Methanes. The procedure recently proposed for the synthesis of tri(1-adamantyl)methane (treatment of the alcohol with oxalyl bromide to give the methyl bromide followed by tributyltin hydride reduction)[10] was used to convert phenyldi-(1-adamantyl)methanols, **3**, **6** and **8**, to the corresponding methanes, which we shall denote as **3-H**, **6-H** and **8-H**. The intermediate bromides were not characterised. Conversion of the *anti,ortho*-tolyl derivative, **4A**, to hydrocarbon resulted in a small yield of a single product with unusual ^1H and ^{13}C NMR shifts for the new CH group. This material was stable to treatment at 250 °C in toluene for 8 h.

Isomerically pure *meta*-substituted alcohols gave isomerically mixed products, **5A-H**, **5S-H** (ratio: 0.67) and **7A-H**, **7S-H** (ratio: *ca.* 1.5), which were only partially separated by crystallisation from hexane and dichloromethane, respectively.

NMR Analysis.—While the *ortho*-tolyl derivatives were easy to identify on the basis of their chromatographic and thermal behaviour, and comparison of their ^1H and ^{13}C NMR spectra with those of the corresponding di(*tert*-butyl)methanols,[11] the *meta* isomers could not be immediately distinguished. For this reason phenyldi(*tert*-alkyl)methanols, **1–3**, were first examined in order to determine the substituent effect of the $-Ad_2COH$ group on the ^{13}C NMR shifts of the aromatic carbons and thereby to predict, by assuming additivity of substituent effects,[12] the shifts of the *meta*-substituted derivatives. The *para*-methyl and *para*-(*tert*-butyl) derivatives, **6** and **8**, were also examined so as to check the validity of the additivity rule in an unambiguous situation.

In the Tables the aromatic carbon and hydrogen atoms are denoted 'a–f' as shown, with 'b' and 'c' on the side of R^1 and 'e' and 'f' on the side of R^2 and R^3.



Inspection of the ^1H NMR of the *anti* and *syn,ortho*-tolyl derivatives (Table 1) reveals a broad doublet at about 8 ppm for the *ortho* proton, H(b), in the *anti*, **4A**, but a broad multiplet at 7.5 ppm, H(f), for the *syn* isomer, **4S**. More generally, for various *meta*- and *para*-substituted phenyldi(*tert*-butyl)-methanols Sternhell[2] found that H(b) resonates 0.14 to 0.25 ppm downfield of **H**(f). The *ortho*-protons in **1**: 7.54 [broad multiplet, **H**(b)] and 7.67 ppm [broad doublet, H(f)] are therefore easily identified. The corresponding carbon atoms are located by a ^{13}C–^1H heteronuclear correlation experiment and the rest of the proton spectrum by a relayed coherence transfer experiment which identifies the nearest neighbour carbon atoms. The *ortho*-proton signals come progressively closer on going from **1** to **2** to **3**, being almost coincident in the last, at 7.55 and 7.59 ppm, respectively. The aromatic carbon atoms in **3** are again assigned by coupling experiments. From **1** to **2** to **3** the shifts of all the aromatic carbons are either almost stationary [C(c) and C(d)] or change regularly by an increment ranging from −0.8 [C(a)] to +0.3 ppm [C(b)] as Bu^t is replaced by Ad.

Unbalanced mixtures of the *meta*-tolyl, **5A** and 5S, or of the *meta*-(*tert*-butyl)phenyl isomers, **7A** and **7S**, obtained directly from the synthesis, showed two distinct sets of six aromatic carbon signals (Table 2) which could be grouped on the basis of their intensities, even before isomer separation. For the *meta*-tolyl isomers, **5A** and **5S**, the other carbon signals were indistinguishable, whereas for the *tert*-butyl isomers, **7A** and **7S**, the Bu^t, Ad-C_q and α-CH_2 shifts were very slightly different (0.06 to 0.17 ppm). The shifts of the aromatic CH carbons were calculated on the basis of the assumption that the substituent effects of the $-Ad_2COH$ group and the methyl or *tert*-butyl substituent are additive. For both the methyl and the *tert*-butyl derivatives a much better fit is obtained if the *syn* and *anti* rotamers are associated with the different groups of aromatic carbon signals as shown. This allows us not only to identify the rotamers but also to assign the carbon signals at the same time.

The ^{13}C spectra of the *anti* and *syn,ortho*-tolyl derivatives, **4A** and **4S**, were completely assigned by comparison with the di(*tert*-butyl) analogues.[11] The aromatic carbon shifts do not obey the additivity rule, the shifts of the CH carbons *ortho* to the two substituents being particularly badly calculated, no doubt because of the severe steric strain on the ring system.

In all cases where correlation experiments have been performed the chemical shift of the *ortho* proton close [H(f)] to the large alkyl groups in the substituent $-CR^2R^3(OH)$ is lower than that of the other, remote proton [H(b)], though the difference may be very small (0.02 ppm for **5A**). Conversely, the shift of the corresponding carbon is always higher than that of the remote one. However, replacing OH by H appears to reverse the situation completely.

The isomeric methanes, **7A-H** and **7S-H**, were identified by ^1H NMR NOE experiments and their ^{13}C spectra (Table 3) assigned by ^1H–^{13}C heteronuclear correlation experiments. Applying the additivity principle in reverse, we then assigned the carbons of the parent, **3**, and thence identified and assigned

Table 1 ^1H and ^{13}C Chemical shifts (ppm/TMS) of phenyldi(*tert*-alkyl)methanols, **1–3**

	δ_H			δ_C		
C or H	**1**	**2**	**3**	**1**	**2**	**3**
a				145.5	144.7	143.9
b	7.67d	7.64d	7.59d	127.3	127.6	127.9
c	7.28		7.28	127.4	127.3	127.3
d	7.18	7.15–7.4	7.19	125.8	125.8	125.7
e	7.18		7.19	125.7	125.5	125.3
f	7.54m	7.54m	7.55m	127.9	128.2	128.4
OH	1.91	[a]	[a]			
C_q–OH				83.1	83.2	83.2
Bu^t	1.09	1.10		29.7, 41.6	30.1, 42.1	—
C_q of Ad				—	44.0	44.7
α-CH_2 of Ad	—			—	39.1	39.4
β-CH of Ad	—	1.5–2.0	1.5–2.0	—	29.1	29.2
γ-CH_2 of Ad	—			—	36.9	37.0

[a] The OH proton is included in the envelope of the Ad signals.

Table 2 ^1H and ^{13}C Chemical shifts (ppm/TMS) of tolyl- and (*tert*-butyl)phenyldi(1-adamantyl)methanols, **4–8**

	4S *syn,ortho*	**4A** *anti,ortho*	**5S** *syn,meta*	**5A** *anti,meta*	**6** *para*	**7S** *syn,meta*	**7A** *anti,meta*	**8** *para*
^{13}C								
a	141.4	144.2	143.7	144.0	140.9	143.2	143.6	140.6
b	138.6	131.1	128.6	125.0	127.8	124.8	124.9	127.3
c	133.4	124.9	136.6	127.1	127.9	149.8	126.7	123.8
d	125.6	126.0	126.2	126.6	135.1	122.0	122.2	148.3
e	122.7	133.0	125.3	134.3	126.3	125.2	147.6	122.4
f	129.8	135.5	125.6	129.2	128.2	125.7	126.1	128.0
C_q–OH	87.8	87.3	83.2	83.2	83.1	83.3	83.3	83.1
C_q of Ad	46.5	45.6	44.7	44.7	44.7	44.65	44.75	44.7
α-CH_2 of Ad	39.3	39.4	39.5	39.5	39.4	39.4	39.5	39.4
β-CH of Ad	29.3	29.4	29.2	29.2	29.2	29.2	29.2	29.2
γ-CH_2 of Ad	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0
Me	26.3	29.5	22.0	22.0	20.9	—	—	—
Bu^t	—	—	—	—	—	31.5, 34.7	31.4, 34.5	31.4, 34.2
^1H								
Ar	7.1–7.2, 7.50m[a]	7.1–7.2, 8.03d[b]	7.0–7.2, 7.3–7.4	7.04d,[c] 7.20t,[d] 7.36s,[a] 7.38d[b]	7.0–7.15, 7.35–7.5	7.1–7.25, 7.36dt,[a] 7.66t[b]	7.2–7.25, 7.38,[a] 7.59br s[b]	7.2–7.3, 7.4–7.5
Ad	1.5–2.1	1.5–2.1	1.5–2.0	1.5–2.0	1.5–2.0	1.5–2.0	1.5–2.0	1.5–2.0
Me	2.60	2.73	2.35	2.39	2.34	—	—	—
Bu^t	—	—	—	—	—	1.32	1.35	1.32

[a] H(f). [b] H(b). [c] H(d). [d] H(c).

the *meta*-tolyl methanes, **5A-H** and **5S-H**. The *para*-substituted derivatives, **6-H** and **8-H**, again served as a check. The single methane obtained by the reaction of **4A** could not be identified unambiguously by NMR; its identification as the *syn* isomer, **4S-H**, is based on other evidence.

Thermal Rotation.—Treatment of a mixture of **4A** and **4S** at 245 °C for 7 h (ten half-lives) gave a product consisting almost entirely of the *syn* isomer (99.8%). Thermal equilibration of **5A**/**5S** in $CDCl_3$ at temperatures between 85 and 150 °C gave isomer ratios of 0.75 to 0.82, corresponding to a free energy difference 0.20 ± 0.03 kcal mol^{-1} in favour of the *syn* isomer; for **7A**/**7S** the ratio was 1.6–1.5, corresponding to a difference of 0.33 ± 0.02 kcal mol^{-1} in favour of the *anti* isomer.

A somewhat approximate determination of the barrier to rotation about the sp^2–sp^3 bond in **5** and **7** gave values of about 27.5 kcal mol^{-1}, this being almost 12 kcal mol^{-1} below that (39.1 kcal mol^{-1} at 200 °C)[6] for the corresponding *anti,ortho*-tolyl derivative, **4A**. A rather smaller difference in rotation barriers occurs for the phenyl- and the *anti,ortho*-tolyldi(*tert*-butyl)methanols (21.4 kcal mol^{-1} and 29 kcal mol^{-1}, respectively, both at 148 °C).[1,5] The activation entropies for the rotation of **2** and **3**, though not known with any great precision, are of the same order of magnitude as those determined previously for analogous compounds.[5,6]

Thermal equilibration of the *meta*-tolyldiadamantylmethanes, **5A-H** and **5S-H**, at temperatures between 100 and 150 °C gave mixtures with *anti*/*syn* ratios of about 0.82, corresponding to a free energy difference of 0.15 kcal mol^{-1}. For the *meta*-(*tert*-butyl) derivatives, **7A-H** and **7S-H**, the ratio was approximately the same but in the other direction, the *anti* isomer being now stabler than the *syn* by about 0.16 kcal mol^{-1}. Rotation rates for the *meta*-tolyl derivatives (starting with a sample containing about 77% of the *syn* isomer, **5S-H**) at 100–130 °C give activation energies approximately 0.5 kcal mol^{-1} greater than those for the corresponding alcohol.

Base-catalysed Rotation of Alcohols.—When alcohols **5** and **7** are treated with butyllithium in hexane equilibrium mixtures are obtained regardless of the initial isomer; for **7A**/**7S** the equilibrium lies heavily on the side of the *anti* rotamer, with the *anti*/*syn* ratio of about 30, whereas for **5A**/**5S** the isomer ratio again favours the *anti* isomer but to a much lesser extent (1.3). The *ortho*-tolyl alcohols, **4A** and **4S**, were not observed to undergo organolithium-catalysed equilibration.

Table 3 ^1H and ^{13}C Chemical shifts (ppm/TMS) of phenyl-, tolyl- and (*tert*-butyl)phenyldi(1-adamantyl)methanes, **3-H–8-H**.

	3-H	**4S-H** *syn,ortho*	**5S-H** *syn,meta*	**5A-H** *anti,meta*	**6-H** *para*	**7S-H** *syn,meta*	**7A-H** *anti,meta*	**8-H** *para*
^{13}C								
a	142.4	141.2	142.26	142.32	139.2	141.8	141.9	139.0
b	133.8	137.8	134.6	131.0	133.7	131.3	130.8	133.3
c	127.0	130.0	136.2	126.7	127.6	149.5	126.3	123.5
d	125.2	124.9	125.8	126.0	134.5	121.5	121.6	147.7
e	126.2	124.0	126.1	135.4	127.1	125.6	148.5	123.2
f	129.5	130.2	126.6	130.3	129.3	126.6	127.2	129.0
C–H	69.6	60.7	69.6	69.4	69.1	70.1	69.4	69.0
C_q of Ad	38.7	39.7	38.7	38.7	38.7	38.7	38.8	38.7
α-CH_2 of Ad	43.4	43.1	43.4	43.4	43.4	43.3	43.5	43.3
β-CH of Ad	29.3	29.3	29.2	29.2	29.2	29.3	29.3	29.3
γ-CH_2 of Ad	37.0	37.1	37.0	37.0	37.0	37.1	37.1	37.1
Me	—	22.2	21.5	22.0	21.0	—	—	—
Bu^t	—	—	—	—	—	31.4, 34.3	31.4, 34.5	31.5, 34.2
^1H								
Ar	6.90m,[a] 7.1–7.3, 7.36t[b]	7.0–7.15, 7.32m[b]	6.72s, 6.9–7.2	6.70dt, 6.9–7.2	6.79dd,[a] 6.99d,[c] 7.04d,[d] 7.23dd,[b]	6.91br s,[a] 7.1–7.2	6.71dt,[a] 7.1–7.2, 7.39t[b]	6.79d,[a] 7.15d,[c] 7.21d,[d] 7.24d[b]
Ad	1.5–2.0	1.5–2.0	1.5–2.0	1.5–2.0	1.5–2.0	1.5–2.0	1.5–2.0	1.5–1.9
Me	—	2.32	2.30	2.37	2.32	—	—	—
Bu^t	—	—	—	—	—	1.30	1.34	1.31
C–H	1.95	2.49	1.93	1.93	1.93	1.93	1.94	1.90

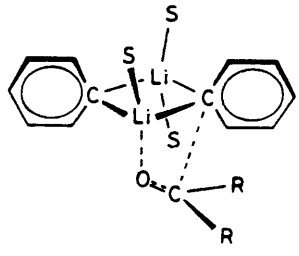
[a] H(b). [b] H(f). [c] H(c). [d] H(e).

Discussion

Crystallographic[13] and solution NMR[14,15] studies now appear to give a coherent picture of the structure of phenyl- and other organo-lithium compounds.[16] Monomers, dimers, tetramers and hexamers may occur, depending on steric bulk, charge delocalisation, solvent polarity, the ligand (such as TMEDA) and the temperature. Phenyllithium–diethyl ether complexes are tetramers even in the presence of excess ether, though *ortho*-methyl substituents favour a dimeric structure.[14] Dimer and tetramer complexes of organolithiums with THF have been reported, but in THF solution many organolithium reagents are partially or completely monomeric.

Less progress has been made towards determining the nature of the species active in addition to carbonyl compounds or the stereochemistry of the reaction. According to *ab initio* calculations[17] the transition structure for the reaction of methyllithium, as the monomer or the dimer, with formaldehyde is very early and is dominated by lithium cation complexation with oxygen. Heavy atom KIE studies on the reaction of methyllithium with benzophenones, however, are held to support an initial SET, which is followed by carbon–carbon bond formation.[18] The two studies agree that the geometrical change of the carbonyl compound is negligible.

The major problem in attempting to interpret our results is to understand how the phenyl ring approaches the carbonyl carbon and how its orientation depends on the substituents. In previous work on *ortho*-tolyldi(*tert*-butyl)methanols[5] we suggested that it must lie in the mirror plane of the ketone, failing which only the *syn* isomer could be formed. This model can now be revised. The *ab initio* calculations depict a planar transition state for dimer addition to formaldehyde (the four-membered ring of the dimer and the carbonyl bond being coplanar). However, it is suggested that in solution the carbonyl oxygen first replaces a solvent molecule, the two carbon atoms (of the carbonyl and the organolithium) coming together subsequently.[17] Models suggest that the four-membered ring would then be not far from orthogonal to the plane which includes the carbonyl and the reacting Li–C bond. If we consider the case of phenyllithium addition, assuming for the sake of simplicity that it is the dimer which reacts, this situation puts the phenyl ring at a somewhat smaller angle to the reference plane, one edge lying in the cleft between the alkyl groups of the ketone. Since the transition state is early it is then possible that the preferential formation of the less stable *ortho*-tolyl derivative is due to a predominance of attractive interactions between the methyl and the large alkyl groups.



For both the *meta*-alkyl substituents examined in this work the *syn* isomer is favoured, but by a much greater extent for *tert*-butyl, **7**, than for methyl, **5**. The transition state geometry suggested by the *ab initio* calculations, the crystallographic studies and molecular models has not only the *ortho*- but also the *meta*-substituent directed towards the alkyl groups of the ketone, the methyl groups of the *tert*-butyl being in the vicinity of the α-CH_2 of the adamantyls. Whether the distances correspond to repulsive or attractive interactions is something which could perhaps be determined by more refined computer modelling studies. The reaction of variously substituted phenyllithiums with di(*tert*-alkyl) ketones in the presence of different solvents and ligands could also be envisaged as a probe for the investigation of the reaction mechanism, but this is beyond the scope of the present study.

Though the species involved have little resemblance to the transition state for RLi addition to ketones, the effects of organolithiums on the alcohols show strikingly how an apparently remote substituent can interact with the oxygen function. Leaving the *meta*-(*tert*-butyl)phenyl alcohols, **7**, as the lithium alkoxide in ether or treating either rotamer with butyllithium in hexane leads to a marked predominance of the *anti* isomer. The *anti*/*syn* ratio for the *meta*-tolyl derivatives, **5**, is unaffected in ether but shifts in favour of the *anti* isomer,

though much less than for *meta*-(*tert*-butyl), when subjected to concentrated BuLi in hexane. This clearly shows that the lithium alkoxide/organolithium aggregate is sufficiently space-demanding for there to be interaction with the *meta*-alkyl group in the *syn* isomer and the rotation to *anti* is favoured, both kinetically and thermodynamically, this interaction being naturally greater for Bu^t than for Me. In the organolithium-catalysed rotation of *ortho*-tolyldi(*tert*-butyl)methanols[5] both k_a and k_s were found to vary linearly with the organolithium concentration, the organolithium not only increasing the rotation rate by a factor of more than 10^5 but also shifting the equilibrium towards the *anti* isomer as the BuLi concentration is increased. This result is consistent with the idea of a progressive expansion of the alkoxide aggregate, increasing its interaction with the *syn*,*ortho*-methyl group and thus favouring the normally less stable *anti* isomer.

It is hardly surprising that the *ortho*-tolyldiadamantylmethanols are unaffected by butyllithium; the barrier for thermal rotation is almost 20 kcal mol^{-1} higher than for the di(*tert*-butyl) derivative[6] which means that, even allowing for a factor of 10^5–10^6, the rate constant for rotation at the highest BuLi concentration at 25 °C would be of the order of 10^{-8} s^{-1}.

Though the NMR spectra gave no indication as to the structure of the methane obtained from *anti*,*ortho*-tolyl alcohol, **4A**, the fact that it is recovered unchanged after 8 h at 250 °C clearly indicates that it is the *syn* isomer, **4S-H**. The *anti* alcohol, **4A**, is completely converted to *syn* by a similar treatment. If **4H** were *anti* it would be expected to isomerise under these conditions, the rotation barrier for the hydrocarbon being little greater than that of the corresponding alcohol, according to the results with **5** and **5-H**, and the *syn* methane being about 6 kcal mol^{-1} more stable than the *anti*, according to molecular mechanics calculations (see below).

Previously, it was found that only the *anti*,*ortho*-tolyldi(*tert*-butyl)methanol gave *para*-nitrobenzoate.[19] We concluded that it had the same conformation as the parent alcohol but a subsequent crystallographic study[20] showed it to be the *syn* isomer. It seems likely that this is due to lowering of the rotation barrier by ground state strain.

The fact that **4A** is converted to **4S-H** and that isomerically pure alcohols, such as **5S** or **7A** and **7S**, give mixed methanes is, however, probably not due to strain in the intermediate bromides* but to loss of isomeric identity in the transition states for formation of the bromides and their reduction. The reaction of oxalyl bromide probably goes through an oxalyl monobromide ester which decomposes to give a carbocation and bromide.[21] It could also be conceived as going *via* a concerted mechanism in which the halogen is delivered to the carbon centre as the C–O bond breaks. The ^{1}H NMR spectra of the crude bromides obtained from **7A** and **7S** were identical, but showed three resonances in the *tert*-butyl region. The ^{13}C spectra show two peaks for each of the adamantyl CH_2 groups and a poorly resolved mass of aromatic carbons. In any case, since tributyltin hydride reduction goes through a disubstituted benzyl radical intermediate[22] the isomer ratios will reflect the small difference in the activation energies for transfer of hydrogen from the hydride to the radical. It is interesting to note that the isomeric preferences of this reaction are retained, though slightly diminished, when the methanes are equilibrated in chloroform.

Molecular mechanics calculations[23] have already been used to estimate the relative energies of the *ortho*-tolyl rotamers,[5] **4A** and **4S**, predicting that the *syn* is the stabler by some 6 kcal mol^{-1}. Calculations with the more recent force field, MMP2,[24] raise this figure to 7 kcal mol^{-1} which would indicate that at 245 °C the equilibrium constant is 10^3 and therefore that 0.1% of the *anti* isomer should remain at equilibrium. Given that ten half-lives implies that there will be 0.1% of the starting material remaining after an irreversible reaction, our NMR figure of 0.2% is fully compatible with this calculation. The lower stability of the *anti* isomer is clearly the result of strong repulsive interactions between the methyl group and the adamantyls.

MMP2 calculations on the *meta*-substituted alcohols suggest that for both the methyl and the *tert*-butyl isomer pairs the *anti*,*meta* should be more stable than the *syn*,*meta*, the difference being about 0.2 and 1.1 kcal mol^{-1} for Me and Bu^t, respectively. Inspection of the various contributions to the calculated steric energies indicates that the predicted differences between isomers are attributable mainly to attractive interactions between the *meta* substituent and the adamantyl groups in the *anti* isomers. In practice we find that the *syn*,*meta*-tolyl, **5S**, is stabler by about 0.2 kcal mol^{-1} and *anti*,*meta*-(*tert*-butyl)phenyl, **7A**, by about 0.3 kcal mol^{-1}. MMP2 thus errs in favour of the *anti* isomer in both cases, the error being slightly greater for Bu^t than for Me.

In the case of the *meta*-tolyl methanes the error is only 0.3 kcal mol^{-1}, MMP2 again favouring *anti*, by 0.15 kcal mol^{-1} while experiment shows the *syn*, **5S-H**, to be stabler by this amount. Calculation gives the right answer for the *tert*-butyl derivatives, but again exaggerates the tendency, predicting that **7A-H** will be 0.75 kcal mol^{-1} more stable than **7S-H**, whereas the difference is only 0.16 kcal mol^{-1}. The error is, however, smaller than for the corresponding alcohols.

Calculations with the still more recent MM3 force field (1989 version),[25] which handles interactions between non-bonded atoms rather differently from MMP2, has little effect upon the predictions for methyl derivatives but reduces the difference between rotamers for the *tert*-butyl-substituted alcohols and methanes, improving therefore the overall agreement between theory and experiment. In all cases the *anti* isomer is predicted to be the more stable, the greatest errors being 0.35 and 0.25 kcal mol^{-1} for the *meta*-(*tert*-butyl)phenyl alcohols and methanes, respectively.

It was expected that the rotation barrier for the hydrocarbons would be greater than that of the alcohols, since the ground state energy is substantially lower, while that of the transition state should be only slightly reduced. In fact, the difference was much smaller than in previous work on 9-arylfluorenes,[26] the rotation barrier for **5-H** being only about 0.5 kcal mol^{-1} greater than that for **5** itself. This is probably because the energies of both the ground states and the rotation transition states are determined to a very large extent by the interactions of the adamantyl groups with the benzene ring.

For the sake of simplicity and rapidity we took the phenyl derivatives as models of the *meta*-substituted alcohols and methanes, assuming that the *meta* substituents have little effect upon the rotation rates, which is a fair approximation to the truth. The transition state for the rotation of a phenyldiadamantylmethane or methanol, $PhAd_2CX$, should, according to previous calculations on rotation barriers for this type of compound,[6,27] correspond to a conformation in which the C–H or C–OH bond is orthogonal to the plane of the benzene ring. Calculations using the DRIVER option in MMP2 with the two dihedral angles involving the C–X bond and the *ortho*-carbons set to 90° and −90° gave rotation barriers of 26.7 and 25.4 kcal mol^{-1} for X = H and OH, respectively.† The

* Rough MM calculations (MMP2 is not adequately parametrised) suggest that the rotation barrier is reduced by less than 1 kcal mol^{-1} when C–OH is replaced by C–Br.

† The DRIVER option does not give the true transition state but describes a point slightly before or after it where one adamantyl group is approximately staggered with respect to the sp^2–sp^3 bond while the other is rotated by about 20°. As the two adamantyl groups exchange conformations on crossing the barrier the true transiton state must have C_{2v} symmetry.

difference is only slightly greater than that found experimentally for the activation enthalpies (average values 25.3 and 24.9 kcal mol^{-1} for methanes and alcohols, respectively) and, moreover, these values are in remarkably good numerical agreement with what is observed. Further calculations on symmetrical phenyldialkylmethanols, PhR_2COH, where R = Pr^i and Bu^t, gave values of 9.7 and 20.8 kcal mol^{-1}, respectively, again compatible with the NMR-determined rotation activation enthalpies (approx 10.2 and 18.9 kcal mol^{-1}).* MM2 generally reproduces rotation barriers for ring compounds fairly well but underestimates them by a large margin for small open-chain systems;[10,28] it now appears to perform remarkably well for congested aryl groups, despite the rather rough calculational method employed.

Conclusions

Provided the rotation of the aryl group about the sp^2–sp^3 bond between the ring and a carbon-centred substituent lacking rotational symmetry is slow, there are five distinct positions for a second, rotationally symmetrical substituent. We have shown that a methyl group can play the role of this second substitutent when the first is the di(1-adamantyl)methanol group. In the same way, two *meta*-(*tert*-butyl)phenyl derivatives can be prepared, but we have not sought to prepare the *ortho*-substituted derivatives, which are probably too strained to be accessible, nor to be exhaustive in our choice of substituents. The various methanols are readily converted into the corresponding methanes with, however, loss of isomeric purity for the *meta*-substituted derivatives and transformation of the *anti,ortho*-tolyl derivative to the stable *syn,ortho*-tolyl methane. The activation enthalpies for the thermal rotation for some phenyldialkylmethanols and phenyldiadamantylmethane are reproduced unusually well by MMP2 calculations. Certain aspects of the transition state for organolithium addition to ketones and the organolithium-catalysed rotation of the alcohols remain obscure and require further study.

Experimental

General Methods.—NMR measurements were made on a Bruker AS 200 FT instrument operating at 200 MHz (^1H) or 50 MHz (^{13}C). All measurements were made in $CDCl_3$ (but for two experiments with *o*-tolyl derivatives in [$^2H_8$]toluene) and are referenced to internal $SiMe_4$ (δ = 0.00 for ^1H) or to the solvent (δ = 77.0 for ^{13}C). Abbreviations used in the Tables are: br = broad; d = doublet; dd = double doublet; dt = double triplet; m = multiplet; s = singlet; t = triplet. A range indicates a broad multiplet. The aromatic carbons and hydrogens in **1**, **3**, **5A**, **3-H**, **4-H**, **5-H**, **6-H**, **7-H** and **8-H** were assigned with the help of ^{13}C–^1H heteronuclear correlation experiments and, in the case of **7-H**, the two isomers were differentiated by proton–proton NOE experiments (performed at University College London). The carbons of the other *meta* and *para* derivatives were assigned by assuming additivity of the effects of the $-Ad_2COH$ or $-Ad_2CH$ and Me or Bu^t groups. For this purpose aromatic carbon shifts measured on our instrument were used: Bu^t: 125.2 (*ortho*), 125.4 (*para*), 128.0 (*meta*), 151.0 (*ipso*); Me: 125.3 (*para*), 128.2 (*meta*), 129.0 (*ortho*), 137.8 (*ipso*). For the determination of *anti*/*syn* ratios the entire reaction products was dissolved in dichloromethane, an aliquot taken and the solvent evaporated at room temperature prior to re-solution in $CDCl_3$. The *anti*/*syn* ratios in synthesis experiments were reproducible to ±8% or better, which corresponds to ± 1–2% on the percentage values. Melting points were determined in capillary glass tubes on a Mettler FP5 instrument with a heating rate of 3 °C min^{-1}.

Alcohol Synthesis

General Procedure.—The normal procedure was to prepare the organolithium compound by reacting the appropriate aryl bromide (10 mmol) in dry diethyl ether (35 dm^3) with excess chopped Li metal (0.05 g at; 1% sodium) magnetically stirred in diethyl ether (15 dm^3) under argon at room temperature.[9] After completion of the reaction (dulling of the metal surface) a solution of di(*tert*-alkyl) ketone (3.4 mmol in diethyl ether (35 dm^3) was added in about 5 min. The reaction mixture was then stirred for a further 0.5 h (unless otherwise stated) before filtration through a glass wool plug, quenching in water, hexane extraction, drying over $MgSO_4$ and evaporation of the solvent. Alcohols were purified by column chromatography on alumina in light petroleum–diethyl ether mixtures and were recrystallised from hexane.

anti/syn *Dependence on Reaction Time for* **4**, **5** *and* **7**.—The appropriate bromide (4.5 mmol) in diethyl ether (15 dm^3) was added dropwise to lithium metal (0.1 g, 14 mg at) in diethyl ether (10 dm^3) under argon. After stirring for 30 min di(1-adamantyl) ketone (0.5 g, 1.7 mmol) in diethyl ether (30 dm^3) was added in 5 min. Samples (5 dm^3) were syringed out at intervals and quenched with water and hexane. The alcohols were isolated by column chromatography and then analysed by NMR. Results were as follows {alcohol: [*t*, *anti* (%)]}. **4**: 2 min, 91; 15 min, 92; 1 h, 92; 4 h, 93; 24 h, 93. **5**: 2 min, 44; 15 min, 43; 1 h, 44; 4 h, 42; 48 h, 43. **7**: 5 min, 17; 1.5 h, 27; 48 h, 63; 72 h, 62. The complement is the *syn* isomer.

(1-*Adamantyl*)(tert-*butyl*)*phenylmethanol*, **2**. Yield 66%, m.p. 77–78 °C (Found: C, 84.6; H, 10.2. $C_{21}H_{30}O$ requires C, 84.51; H, 10.13%).

Di(1-*adamantyl*)*phenylmethanol*, **3**. Yield 47%, m.p. 211 °C (lit.,[8] 212.4 °C) (Found: C, 86.3; H, 9.5. $C_{27}H_{36}O$ requires C, 86.11; H, 9.64%).

anti-*Di*(1-*adamantyl*)-o-*tolylmethanol*, **4A**. Yield 61%, m.p. 199 °C (Found: C, 86.2; H, 9.9. $C_{28}H_{38}O$ requires C, 86.10; H, 9.81%).

syn-*Di*(1-*adamantyl*)-o-*tolylmethanol*, **4S**. Yield 4%, m.p. 177 °C (Found: C, 86.2; H, 9.6. $C_{28}H_{38}O$ requires C, 86.10; H, 9.81%). Better yields (37%) are obtained by heating **4A** in dodecane in a sealed tube at 245 °C for 2 h, followed by chromatography and recrystallisation.

anti-*Di*(1-*adamantyl*)-m-*tolylmethanol*, **5A**. Obtained from the mother-liquors of four syntheses by 10–12 crystallisations from hexane. Yield 2% (99.9% isomerically pure), m.p. 213 °C (Found: C, 86.0; H, 9.9. $C_{28}H_{38}O$ requires C, 86.10; H, 9.81%).

syn-*Di*(1-*adamantyl*)-m-*tolylmethanol*, **5S**. Yield 11% (99.7% isomerically pure after 6 recrystallisations), m.p. 213 °C (Found: C, 85.9; H, 9.8. $C_{28}H_{38}O$ requires C, 86.10; H, 9.81%).

Di(1-*adamantyl*)-p-*tolylmethanol*, **6**. Yield 32%, m.p. 277–278 °C (lit.,[8] 274.7 °C) (Found: C, 86.2; H, 9.9. $C_{28}H_{38}O$ requires C, 86.10; H, 9.81%).

anti-*Di*(1-*adamantyl*)-m-(tert-*butyl*)*phenylmethanol*, **7A**. Reaction time: 72 h. Yield 58% (99.8% isomerically pure after one recrystallisation), m.p. 185–187 °C (Found: C, 86.4; H, 10.4. $C_{31}H_{44}O$ requires C, 86.05; H, 10.25%).

syn-*Di*(1-*adamantyl*)-m-(tert-*butyl*)*phenylmethanol*, **7S**. Re-

* It is somewhat difficult to estimate these values since the measurements were made on the 3,4,5-trimethoxy derivatives and only the activation energies were determined.[1] Previous experience[5] suggests that the 4-methoxy group lowers the activation energy by about 0.4 kcal mol^{-1}; we ignore the effect of the *meta*-substituents; in the light of data in this paper and elsewhere,[5,6] the activation entropy can reasonably be attributed a value of about -7 cal mol^{-1} K^{-1}.

action time: 5 min. Yield 37% (99.6% isomerically pure after two recrystallisations), m.p. 185–187 °C (Found: C, 85.9; H, 10.3. $C_{31}H_{44}O$ requires C, 86.05; H, 10.25%).

Di(1-*adamantyl*)-p-(tert-*butyl*)*phenylmethanol*, **8**. Yield 46%, m.p. 271 °C (Found: C, 86.1; H, 10.3. $C_{31}H_{44}O$ requires C, 86.05; H, 10.25%).

Methane Synthesis

General Procedure.—Treatment of an alcohol (1 g, 2.3–2.7 mmol) with a large excess of oxalyl bromide (3.2 g, 15 mmol) in benzene (50 dm^3) for 2–3 days at room temperature gave the corresponding bromide, which was isolated by pumping off the solvent and excess reactant at room temperature. The crude bromide was converted into the corresponding methane by refluxing it in benzene (50 dm^3) with AIBN (20 mg) and excess tributyltin hydride (1.3 g, 4.4 mmol) for 1–2 h.[10] The methanes were isolated by alumina chromatography in light petroleum.

Di(1-*adamantyl*)*phenylmethane*, **3-H**. Yield 58%, m.p. 213 °C (Found: C, 90.1; H, 10.1. $C_{27}H_{36}$ requires C, 89.94; H, 10.06%). The crude bromide had δ_C 29.7 (CH), 36.8 (CH_2), 39.4 (weak, CH_2), 48.1 (C_q), 110.8 (C-Br), 125.0, 126.6, 127.5, 128.7, 135.4, 140.7 (Ar), together with peaks corresponding to residual alcohol and unknown impurities.

syn-*Di*(1-*adamantyl*)-o-*tolylmethane*, **4S-H**. By reaction of the *anti* alcohol, **4A**: yield 18%, m.p. 148 °C (Found: C, 90.0; H, 10.4. $C_{28}H_{38}$ requires C, 89.77; H, 10.23%).

anti- *and* syn-*Di*(1-*adamantyl*)-m-*tolylmethanes*, **5A-H** *and* **5S-H**. From **5S**: after chromatography the material had an *anti*/*syn* ratio of 0.67. One crystallisation from hexane gave a solid with *anti*/*syn* ratio of 0.29 (0.34 g, 35%) while the mother liquor yielded 0.33 g (34%) with a ratio of 1.35. M.p. 202 °C (solid) (Found: C, 89.8; H, 10.3. $C_{28}H_{38}$ requires C, 89.77; H, 10.23%).

Di(1-*adamantyl*)-p-*tolylmethane*, **6-H**. Yield 70%, m.p. 254–255 °C (Found: C, 89.6; H, 10.4. $C_{28}H_{38}$ requires C, 89.77; H, 10.23%).

anti- *and* syn-*Di*(1-*adamantyl*)-m-(tert-*butyl*)*phenyl methanes*, **7A-H** *and* **7S-H**. After chromatography the material had an *anti*/*syn* ratio of 1.6. A solution in dichloromethane was allowed to evaporate to dryness; crystalline material (0.47 g, 49%) recovered from the walls of the flask had an *anti*/*syn* ratio of 4.3, while powder recovered from the bottom (0.42 g, 44%) had an *anti*/*syn* ratio of 0.63. M.p. 198 °C (cryst.) (Found: C, 89.6; H, 10.7. $C_{31}H_{44}$ requires C, 89.36; H, 10.64%).

Half-scale experiments on **7A** and **7S** gave methanes in yields (after chromatography only) of 89% (*anti*/*syn* ratio: 1.54, *i.e.* 60.5% *anti*) and 91% (*anti*/*syn* ratio: 1.35, *i.e.* 57.4% *anti*). The crude bromides had identical ^1H NMR spectra with three (*sic*) Bu^t signals, at 1.32, 1.33 and 1.35 ppm. δ_C 29.2 (CH or CH_3), 29.8 (CH_3 or CH), 31.4 (CH_3), 34.6 (C_q), 36.8 (CH_2), 37.0 (CH_2), 39.4 (CH_2), 39.5 (CH_2), 44.7 (C_q), 48.1 (C_q), 110.8 (C-Br) and 12 or more poorly resolved Ar carbons from 122.2 to 147.1 ppm.

Di(1-*adamantyl*)-p-(tert-*butyl*)*phenylmethane*, **8-H**. Yield 49%, m.p. 234–235 °C (Found: C, 89.8; H, 10.6. $C_{31}H_{44}$ requires C, 89.36; H, 10.64%).

Thermal Rotation Kinetics and Equilibria

Alcohols.—Solutions of the *syn,meta* isomers, **5S** and **7S** (*ca.* 50 mg in 5 dm^3 $CDCl_3$) were divided into ten 0.5 dm^3 aliquots and sealed under vacuum in glass ampoules. Each set was placed in a thermostat at temperatures between 85 and 117.5 °C; eight samples were withdrawn and cooled rapidly to room temperature at appropriate time intervals spanning 2–3 reaction half-lives while the remaining two were left for 10 half-lives. The *anti*/*syn* ratio was determined for each sample by ^1H NMR. Overall rate constants ($k_a + k_s$, where k_a is the constant for conversion of *anti* to *syn* and k_s the opposite) and equilibrium constants, k_a/k_s, were as follows (alcohol, T/°C, $k_a + k_s/s^{-1}$, k_a/k_s): **5**, 85.1, 2.30×10^{-4}, 1.27; 100.3, 9.65×10^{-4}, 1.25; 117.5, 4.59×10^{-3}, 1.31; **7**, 85.1, 2.80×10^{-4}, 0.637; 100.3, 9.87×10^{-4}, 0.656; 117.5, 5.53×10^{-3}, 0.631. Given the fact that only one run was performed for each compound at each temperature (for reasons of economy), that the final percentage of *syn* isomer is known to about ± 1–2% and that there is some scatter about the first-order regression line, the individual rate constants are known to about ± 5–15% only. This represents an uncertainty of some 0.04–0.10 kcal mol^{-1} on the activation energies. Activation enthalpies and entropies for rotation are as follows (alcohol, $\Delta H^{\ddagger}$/kcal mol^{-1}, $\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}): **5A**, 25.1 ± 0.5, −6.7 ± 1.3; **5S**, 24.8 ± 0.2, −8.0 ± 0.4; **7A**, 24.9 ± 1.8, −7.6 ± 4.8; **7S**, 25.0 ± 2.1, −6.5 ± 5.7.

The differences in the free energies of formation of the rotamers were calculated from the equilibrium constants at various temperatures between 85 and 150 °C. **5A**/**5S**, **7A**/**7S** (T/°C): 0.746, 1.58 (85.1); 0.763, 1.56 (100.3); 0.781, 1.54 (117.5); 0.775, 1.51 (135.0); 0.82, 1.49 (150.0). The free energy differences showed no systematic variation with the temperature: $\Delta\Delta G°$ (**5A** − **5S**) = 0.20 ± 0.03 kcal mol^{-1}; $\Delta\Delta G°$ (**7S** − **7A**) = 0.33 ± 0.02 kcal mol^{-1}.

A sample of the *anti*-diadamantyl-*o*-tolylmethane, **4A**, was heated in [$^2H_8$]toluene for 7 h at 245 °C. ^1H NMR indicated that there was approximately 0.2% residual **4A**, the remainder being **4S**.

Methanes.—The rotation kinetics of the **5-H** system were determined in the same way as above at 100–130 °C using as starting material a sample with an *anti*/*syn* ratio of 0.29 (77% *syn*). Overall rate constants ($k_a + k_s$, where k_a is the constant for conversion of *anti* to *syn* and k_s the opposite) and equilibrium constants, k_a/k_s, were as follows (T/°C, $k_a + k_s/s^{-1}$, k_a/k_s): 99.9, 4.99×10^{-4}, 1.23; 114.8, 1.70×10^{-3}, 1.22; 129.9, 6.80×10^{-3}, 1.21. Activation enthalpies and entropies are as follows (rotamer, $\Delta H^{\ddagger}$/kcal mol^{-1}, $\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}): **5S-H**: 25.4 ± 1.4; −7.7 ± 3.7; **5A-H**, 25.2 ± 1.4, −7.8 ± 3.6.

From the data obtained in the kinetic experiments the free energy difference between the two isomers, $\Delta\Delta G°$ (**5A-H** − **5S-H**) was found to be 0.15 ± 0.01 kcal mol^{-1}. Kinetics were not performed on **7-H** but thermal equilibration of 10 mg samples in $CDCl_3$ (0.5 dm^3) in sealed tubes at 100–150 °C gave **7A-H**/**7S-H** = 1.23 (100 °C); 1.23 (125.1 °C); 1.21 (150.0 °C), corresponding to a free energy difference, $\Delta\Delta G°$ (**7S-H** − **7A-H**), of 0.16 ± 0.01 kcal mol^{-1}.

A sample of the methane obtained from the *anti*-diadamantyl-*o*-tolylmethanol, **4A**, was heated in [$^2H_8$]toluene for 8 h at 250 °C. It was recovered unchanged.

Base-catalysed Equilibration of Alcohols

ortho- or *meta*-Substituted alcohols, **4**, **5** and **7** (10 mg) were treated with butyllithium in hexane (1.6 mol dm^{-3}; 3 dm^3) at room temperature for 1 h, then quenched by pouring into a mixture of hexane and ice–water. The hexane layer was separated, washed with water and dried ($MgSO_4$). After evaporation of the solvent and re-solution in $CDCl_3$ the *anti*/*syn* ratios were determined by ^1H NMR: **5**, 1.3; **7**, 30. Neither **4A** nor **4S** was affected by this treatment.

Molecular Mechanics Calculations

Allinger's program MMP2(85)[24] was used without any modification. Some calculations were repeated with the more recent MM3 (1989 version);[25] results are given in parentheses after the MMP2 values. Steric energies (kcal mol^{-1}) for the alcohols and methanes were as follows. Alcohols: **3**; 55.55; **4A**,

68.09 (84.56); **4S**, 61.11 (78.38); **5A**, 54.98 (71.86); **5S**, 55.17 (71.95); **6**, 55.21; **7A**, 58.60 (73.29); **7S**, 59.74 (73.97); **8**, 59.80. Hydrocarbons: **3-H**, 45.97; **4A-H**, 53.18 (73.96); **4S-H**, 47.36 (68.03); **5A-H**, 45.47 (64.10); **5S-H**, 45.62 (64.22); **6-H**, 45.69; **7A-H**, 49.31 (65.63); **7S-H**, 50.06 (66.04); **8-H**, 50.34.

Rotation transition states were modelled by taking the optimised structure, fixing one C_{ortho}–C_{ipso}–C–X angle to 90° with the DRIVER option and optimising, then repeating this operation on the revised structure with the second angle also fixed, at −90°. Steric energies of the transition states were 72.69 and 80.94 kcal mol^{-1} for **3-H** and **3**, respectively. Alcohols $Ph(Pr^i)_2COH$ and $Ph(Bu^t)_2COH$ gave optimised steric energies of 12.54 and 25.53 kcal mol^{-1} and transition states at 22.23 and 46.32 kcal mol^{-1}, respectively.

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