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Synthesis and Very Slow sp^2–sp^3 Rotation of *anti-o*-Tolyldi(1-adamantyl)methane

John S. Lomas*,† and J. Edgar Anderson‡

Institut de Topologie et de Dynamique des Systèmes,
Université de Paris 7, associé au C.N.R.S. (URA 34),
1 rue Guy de la Brosse, 75005 Paris, France, and Chemistry
Department, University College, Gower Street,
London WC1E 6BT, U.K.

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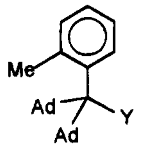
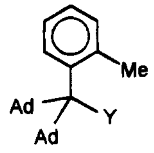
Introduction

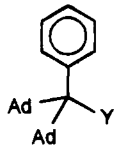
In previous work[1] one of us reported that the reaction of *anti-o*-tolyldi(1-adamantyl)methanol, **1A-OH**, with oxalyl bromide, followed by reduction of the resulting bromide with tri-*n*-butyltin hydride gave in small yield the *syn-o*-tolyldi(1-adamantyl)methane, **1S-H**. According to molecular mechanics calculations, the *syn* rotamer should be about 6 kcal mol^{-1} more stable than the *anti* rotamer, **1A-H**, and our assignment of the isolated methane as the *syn* isomer was based largely on the fact that there was no change under conditions (heating at 250 °C for 8 h) which we believed to be adequate for rotation of the *anti* to the *syn* rotamer. We wish now to report the isolation of *anti-o*-tolyldi(1-adamantyl)methane, **1A-H**, and its remarkably slow thermal rotation to the isomer previously reported. The structures of both isomers are confirmed by NOE experiments.



1A – Y



1S – Y



2– Y

An alcohol can be conveniently deoxygenated by generating the corresponding carbenium ion by means of trifluoroacetic acid in dichloromethane and then reducing it with triethylsilane. This method is sometimes known as "ionic hydrogenation".[2] In a very detailed study of the kinetics of hydride transfer from hydrosilanes to diarylcarbenium ions [generated by means of a Lewis acid ($TiCl_4$, BCl_3 or Me_3SiOTf) at −70 °C], Mayr[3] compared a large number of mono-, di-, and trihydrosilanes bearing various alkyl and aryl substituents. Kinetic isotope effects are in accord with a polar mechanism with rate-determining formation of silicenium ions.

Results and Discussion

The *anti-o*-tolyl alcohol, **1A-OH**, with TFA (10% v/v) in $CDCl_3$ gives a deep orange-red solution (λ_{max} 350 nm; ϵ_{max} 5750 M^{-1} cm^{-1}) whose ^{13}C NMR spectrum indicates complete conversion to the corresponding carbenium ion. The spectrum is analogous to that for related *para*-substituted diadamantylbenzyl cations observed under stable ion conditions at −78 °C in FSO_3H–SO_2ClF mixtures,[4] the chemical shift of the cation center being, however, even greater (303.2 ppm) than those reported by Olah (283.0–287.1 ppm). Again, the aromatic carbons are relatively unaffected by the charge (^{13}C 122.1–139.6 ppm), while the large downfield shift of the C^{α} adamantyl carbons to 70.4 ppm indicates extensive compensatory hyperconjugative interactions. The same carbenium ion is produced much more slowly and incompletely when the *syn-o*-tolyl alcohol, **1S-OH**, is treated in the same way.

Treatment of either *anti*-, **1A-OH**, or *syn-o*-tolyldiadamantylmethanol, **1S-OH**, with TFA and TES in dichloromethane at room temperature gave the same methane in high yield, the reaction of the latter rotamer being, however, substantially slower than that of the former and the color of the reaction mixture being always much lighter than for the *anti* isomer. This suggests that the rates of formation of the carbenium ion from the *syn* isomer and its reduction by the silane are comparable, in contrast to the *anti* isomer where the cation is formed immediately. This is consistent with the energy difference between the two rotamers and previous work on the dehydration of aryldi-*tert*-butylmethanols.[5]

^1H and ^{13}C NMR spectra of the product, *o*-tolyldiadamantylmethane, purified by chromatography on a short alumina column, showed it to be isomeric with the known material,[1] the proton shifts of the methyl hydrogens and the tertiary hydrogen being almost exactly reversed. A NOE experiment on the new isomer **1A-H** showed clearly that the benzylic hydrogen is close to one of the aromatic hydrogens; the same experiment with the known material **1S-H** indicated that the benzylic hydrogen is relaxed in part by the methyl substituent.

The fact that hydride transfer to the *o*-tolyldiadamantylcarbenium ion gives exactly the opposite stereochemical result to hydrogen transfer to the corresponding radical[1] has implications regarding the transition states for these two reactions. The exclusive formation of the *anti-o*-tolyldiadamantylmethane, **1A-H**, shows that, not unexpectedly, the silane delivers hydride to the less hindered side of the carbenium ion. What remains surprising is that in the radical reaction the opposite occurs, also exclusively.

The first-order rate constant for rotation about the sp^2–sp^3 bond in **1A-H** in toluene-d_8 was determined by ^1H NMR comparison of the methyl signal with the methylene of an internal standard, bibenzyl. In the range 257–285 °C, the rotation barrier is 45.1 to 45.4 kcal mol^{-1}, i.e., about 6 kcal mol^{-1} higher than that (39.1 kcal mol^{-1}) for the corresponding alcohol at 200 °C.[6] The activation entropy of −11 cal mol^{-1} K^{-1} is of the same order of magnitude as that determined for related alcohols[1,6] and a hydrocarbon.[1]

In an attempt to model rotation in phenyldiadamantylmethane, **2-H**, and the corresponding alcohol, **2-OH**,[1] in terms of a rather rigid transition state, the benzylic C–H or the C–OH bond was assumed to be at 90° to the plane of the benzene ring. The interactions of this hydrogen or the OH group with the ring should be minimal, but, nevertheless, the calculated steric energy (MMP2)[7] of the transition state for rotation in the alcohol

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[‡] University College.

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(80.9 kcal mol^{-1}) is substantially higher than that for the methane (72.7 kcal mol^{-1}), the difference being almost as great as that between the initial states (55.6 and 46.0 kcal mol^{-1}, respectively). Consequently, molecular mechanics calculations predict only a small difference in the rotation barriers (1.4 kcal mol^{-1}); experimentally it is even less (0.5 kcal mol^{-1}).[1] For the rotation of **1A-H** to **1S-H**, because the aryl group is dissymmetric, no simple assumption can be made about the conformation of the transition state, and modeling with MMP2 by driving one or even two dihedral angles was unsuccessful. It is not possible, therefore, to explain quantitatively why introduction of the *o*-methyl substituent raises the rotation barrier of the alkane so much more than that of the alcohol, though the trend is consistent with earlier ideas about substituent effects on rotation barriers.[8,9]

A qualitative explanation is that the Ad−C−Ad bond angle is smaller in the alcohols than in the alkanes, and this has a double effect on the rotational barriers in these compounds. Compression of this angle by the OH group *increases* interactions between the adamantyl groups and the *o*-methyl in the *anti,ortho* ground state.[10] Proof of this is the difference between the steric energies of the *anti-o*-tolyl derivatives [68.1 (**1A-OH**) − 53.2 (**1A-H**) = 14.9 kcal mol^{-1}] and the corresponding phenyl derivatives [55.6 (**2-OH**) − 46.0 (**2-H**) = 9.6 kcal mol^{-1}].[1] Conversely, pinching this angle *reduces* the interaction between the adamantyl groups and the aryl system in the transition state for rotation in the alcohols as compared to the situation in the alkanes.[11] In short, both ground state and transition state effects tend to favor rotation in the *anti-o*-tolyl alcohol.

Rotation barriers greater than 40 kcal mol^{-1} have been demonstrated before.[9] Oki examined the rotation kinetics and equilibria in *peri*-substituted 9-(1,1-dimethyl-2-phenylethyl)triptycenes and found a maximum value for the rotation barrier of about 43.3 kcal mol^{-1} in the range 227−258 °C when the *peri* substituent was fluoro.[12] The value is slightly greater (44.0 kcal mol^{-1}), due to buttressing, for a tetrafluoro derivative.[13] Systems with potentially higher rotation barriers have been devised, but the barriers have not been measured. For 2,2′-dimethylbitriptycyl,[14] the Arrhenius activation energy for rotation is calculated to be in excess of 54 kcal mol^{-1}, on the basis of the failure to observe rotamer interconversion after 1 week in naphthalene at 300 °C. DL- and *meso*-1,2-di(1-adamantyl)-1,2-di-*tert*-butylethanes[15] are calculated to have rotation barriers in excess of 60 kcal mol^{-1}, but both are readily thermolyzed ($t_{1/2}$ = 1 h at 109−122 °C). The activation energy of about 45 kcal mol^{-1} which we have determined for rotation about the sp^2−sp^3 bond in *anti-o*-tolyldiadamantylmethane, **1A-H**, is the highest reported to date for this type of transformation. Previous experience[16] and recent work[17] suggest that this could be further enhanced by buttressing, as in the prehnityl derivative, for example.

Experimental Section

^{13}C NMR Spectrum of the *o*-Tolyldi(1-adamantyl)methyl Cation. *anti-o*-Tolyldi(1-adamantyl)methanol, **1A-OH** (15 mg), was dissolved in CDCl$_3$ (0.5 mL) in an NMR tube, to which was then added trifluoroacetic acid (0.05 mL). After shaking, a series of JMOD ^{13}C NMR spectra were recorded at 22 °C over periods of 15 mn (100 scans) to 150 mn (1000 scans). The first spectrum, though of relatively poor quality, revealed that all signals associated with the alcohol had disappeared, with the appearance of a new spectrum consistent with a carbenium ion: δ_C 24.6 (Me), 28.5 (6 CH), 34.7 (6 CH$_2$), 41.6 (6 CH$_2$), 70.4 (2 C$_q$), 122.1 (CH), 125.2 (CH), 132.1 (CH), 133.9 (CH), 134.1 (C$_q$), 139.6 (C$_q$), 303.2 (C$^+$). Subsequent spectra showed increasing peaks at 29.2 (CH), 36.8 (CH$_2$), and 39.4 (CH$_2$) ppm, corresponding to the formation of protonated *syn* alcohol. This was confirmed by repeating the experiment with this isomer. Treatment of *syn-o*-tolyldi(1-adamantyl)methanol, **1S-OH**, under the same conditions gave initially a ^{13}C NMR spectrum slightly different from that of the alcohol alone but identical with the minor component of the **1A-OH/TFA/CDCl$_3$** mixture: δ_C 26.0 (Me), 29.2 (6 CH), 36.8 (6 CH$_2$), 39.4 (6 CH$_2$), 46.5 (2 C$_q$), 90.7 (C$_q$), 123.2 (CH), 126.1 (CH), 130.0 (CH), 133.9 (CH), 137.5 (C$_q$), 140.3 (C$_q$). The carbenium ion spectrum built up slowly, reaching a maximum of about 25−30% after 8 h.

Synthesis of *anti-o*-Tolyldi(1-adamantyl)methane, 1A-H. *anti-o*-Tolyldi(1-adamantyl)methanol, **1A-OH** (100 mg, 0.26 mmol), was dissolved in a mixture of dichloromethane (10 mL) and trifluoroacetic acid (1 mL), and to the stirred solution at room temperature was added triethylsilane (0.1 mL; 0.63 mmol). After 4 h, the colorless mixture was quenched with water and washed twice with water, and the dichloromethane solution of the hydrocarbon was dried over MgSO$_4$. Evaporation of the solvent and residual silane gave a product from which the methane was isolated by chromatography on a short alumina column in pentane and recrystallization from hexane. Yield 83 mg (87%); mp 132−3 °C; δ_C (JMOD and XHCORR) 25.6 (Me), 29.4 (6 CH), 36.9 (6 CH$_2$), 39.2 (2 C$_q$), 44.0 (6 CH$_2$), 74.4 (benzylic CH), 124.2 (CH), 125.5 (CH), 131.7 (CH), 136.3 (C$_q$), 137.5 (CH), 141.7 (C$_q$); δ_H 1.5−2.0 (20 H, broad multiplet of Ad), 2.31 (1H, s, benzylic), 2.53 (3H, s, methyl), 6.9−7.1 (4H, multiplet of aromatics). (Found: C, 89.5; H, 10.5. $C_{28}H_{38}$ requires C, 89.77; H, 10.23). The same material was obtained from *syn-o*-tolyldi(1-adamantyl)methanol, **1S-OH**, but about 24 h was required for the reaction to go to completion. Slow reaction with formation of unidentified byproducts was observed in either case when triisopropylsilane was used instead of TES.

NOE Experiments. NOE difference spectra were obtained on deoxygenated solutions (ca. 2%) of **1A-H** and **1S-H** in CDCl$_3$. **1A-H**: irradiation at 2.32 ppm (C−H) gave a large NOE (12.3%) to the aromatic hydrogen at 6.9 ppm (H-6); at 2.53 ppm (CH$_3$), a small NOE (5.0%) to the aromatics (H-3). **1S-H**: irradiation at 2.49 ppm (C−H) gave only a small NOE (2.3%) to the methyl group; at 2.31 ppm (CH$_3$), weak NOEs, 5.5 and 4.3%, to the benzylic and ring hydrogens (H-3), respectively. These results agree with the assignments.

Thermal Rotation Kinetics. *anti-o*-Tolyldi(1-adamantyl)methane, **1A-H** (20−25 mg), and bibenzyl (ca. 5 mg) were dissolved in toluene-d_8 (0.75 mL), and the solution was divided into 12 approximately equal aliquots (ca. 0.06 mL) which were sealed under vacuum in glass ampules (total volume ca. 0.25 mL). The batch of samples was placed in a thermostat at temperatures between 257 and 285 °C, and samples were withdrawn at appropriate time intervals spanning 2−3 half-

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(10) Calculated Ad−C−Ad bond angles for alcohol **1-OH** and alkane **1-H** are 121.6° and 124.6°, respectively.

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lives. Each sample was diluted with $CDCl_3$ (0.45 mL) for ^1H NMR analysis. First-order rate constants were determined by plotting the logarithm of the ratio of the heights of the bibenzyl CH_2 (2.96 ppm) and the *anti* methyl (2.52 ppm) peaks against time. Unfortunately, the methyl signal of the product *syn* isomer, **1S-H**, at 2.32 ppm is masked by incompletely deuteriated toluene methyl groups, but the smaller benzylic proton signal at 2.48–2.49 ppm was used as a cross-check to ensure that the disappearance of the *anti* isomer was due to rotation and not to decomposition. This last point was confirmed by GC/MS. Rate constants were (T in °C, k in s^{-1}): 257.4, $(3.04 \pm 0.03) \times 10^{-6}$; 269.4, $(6.74 \pm 0.04) \times 10^{-6}$; 284.7, $(1.97 \pm 0.02) \times 10^{-5}$, whence we obtain $\Delta H^{\ddagger} = 39.3 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.0 \pm 2.4$ cal mol^{-1} K^{-1}.

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