Thermal fragmentation of 1-substituted spiro[adamantane-2,2′-adamantane] derivatives

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Thermolysis of 1-hydroxy- or 1-acetoxy[1]diadamantane gives mixtures of 3-(adamantylidene)-bicyclo[3.3.1]non-6-ene, 3, 3-(2-adamantyl)bicyclo[3.3.1]nona-2,6- and -2,7-dienes, 4, and 2-(3-noradamantyl)-2,4-dehydroadamantane, 7. At low conversion 3 and 7 are the major products, while one isomer of 4, the 2,6-diene, predominates in the equilibrium mixture. Pd/C-catalysed hydrogenation of the dienes in ethanol gives first 3-(2-adamantyl)bicyclo[3.3.1]non-2-ene, 5, and then *endo*-3-(2-adamantyl)bicyclo[3.3.1]nonane, 6. Hydrocarbon 7 is not hydrogenated under these conditions; it is converted into a mixture of 3 and 4(2,6) upon heating. Mechanisms for the fragmentation of the 1-[1]diadamantyl carbocation are discussed. While a 1,4-hydride shift may contribute to the reactions of the [1]diadamantane system, molecular mechanics calculations suggest that the ready formation of an olefin from 1-hydroxyspiro[adamantane-2,9′-bicyclo[3.3.1]nonane] is best interpreted in terms of a 1,5-hydride shift involving the chair–boat conformation of the bicyclononane system.

During work on the thermolysis of 2-(*tert*-alkyl)adamantan-2-ols, a reaction which leads to 2-substituted 2,4-dehydroadamantanes,[1] we undertook to study the thermolysis of 2-(3-noradamantyl)adamantan-2-ol, **1**. This behaved rather differently from the other members of the family (where the tertiary alkyl group was 1-adamantyl, 1-bicyclo[2.2.2]octyl or 1-norbornyl), and rearranged to the known 1-hydroxyspiro[adamantane-2,2′-adamantane],[2] (more usually referred to as 1-hydroxy[1]diadamantane,[3] **2-OH**). However, substantial amounts of an elimination product, a diene, were also isolated. The fragmentation of adamantane derivatives to bicyclo[3.3.1]nonanes, frequently followed for synthetic purposes by ring closure, is well documented,[4,5] but previous reports of diene formation involve the reactions of 1,4-disubstituted adamantanes where the leaving group is on a *secondary* carbon; for example, the chromium(II)-promoted fragmentation of 1-bromo-4-adamantyl mesylate[6] and the solvolysis of 1-(trimethylsilyl)- and 1-(trimethylstannyl)-4-adamantyl brosylates.[7]

The unexpected fragmentation of a *tertiary* adamantyl carbocation prompted us to reinvestigate certain aspects of the chemistry of [1]diadamantane which has been little studied since its synthesis by two teams in 1972.[2] Reaction of 2-(3-noradamantyl)adamantan-2-ol, **1**, with 48% aqueous HBr and H_2SO_4 gives a mixture[8] of 1-hydroxy- and 1-bromo[1]diadamantanes, **2-OH** and **2-Br**, which can be converted into [1]diadamantane, **2-H**;[2b,8] this latter has also been synthesized *via* the 4-ketone.[2a] This paper is devoted to the fragmentation of the [1]diadamantane system; the accompanying paper[9] is concerned with the rearrangement of 1-halo[1]diadamantanes to 4-halo derivatives. In an attempt to elucidate the mechanisms of these reactions, spiro[adamantane-2,9′-bicyclo[3.3.1]nonane] derivatives were briefly studied.

Results

Thermal rearrangement and fragmentation of 2-(3-noradamantyl)adamantan-2-ol, 1

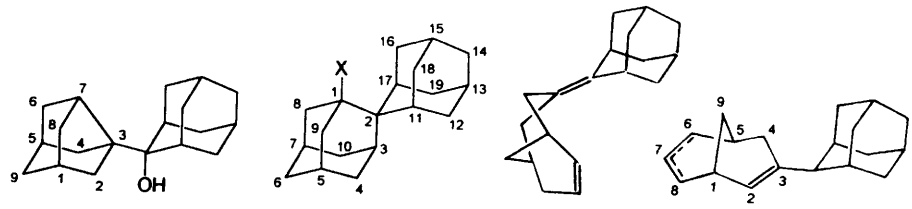
2-(3-Noradamantyl)adamantan-2-ol, **1**, was prepared by the one-pot Barbier-type condensation[10] of 3-bromonoradamantane with adamantan-2-one by means of lithium in diethyl ether. Though this method avoids the preparation of 3-iodonoradamantane, it has the disadvantage that substantial amounts of diol[11] are formed by self-reaction of adamantylketyl radicals.

Thermolysis of 2-(3-noradamantyl)adamantan-2-ol in cumene for 10 h at 280 °C gave 1-hydroxy[1]diadamantane, **2-OH**, and a mixture of hydrocarbons, of which the major component was readily identified. The ITD (Ion Trap Detector), ^{13}C and ^{1}H NMR spectral evidence is consistent with this product being 3-(adamantylidene)bicyclo[3.3.1]-non-6-ene, **3**. Prolonged thermolysis of 2-(3-noradamantyl)-adamantan-2-ol or of 1-hydroxy[1]diadamantane, which amounts to the same thing, gave **3** and two other dienes, in a ratio of about 1:2.5:0.28. The ^{13}C, ^{1}H, XHCORR and COSY NMR spectra of the major component indicate that it is 3-(2-adamantyl)bicyclo[3.3.1]nona-2,6-diene, **4**(2,6), formed by rearrangement of **3**.† The minor component seems likely to be the other 3-(2-adamantyl)bicyclo[3.3.1]nonadiene, **4**(2,7) (for this reason the position of the second double bond in **4** is not fully specified). Partial Pd/C-catalysed hydrogenation of **3** gives 3-(2-adamantyl)bicyclo[3.3.1]non-2-ene, **5**, while complete hydrogenation of a mixture of the three dienes gives a single product, identified by its ^{13}C NMR spectrum and comparison with the spectra of 3-substituted bicyclo[3.3.1]-nonanes[12] and 2-substituted adamantanes[13] as *endo*-3-(2-adamantyl)bicyclo[3.3.1]nonane, **6**. One of the minor components resulting from the thermolysis of **1** was 2-(3-noradamantyl)-2,4-dehydroadamantane, **7**, identified by NMR comparison with other 2-(*tert*-alkyl)-2,4-dehydroadamantanes;[1] this was resistant to Pd/C-catalysed hydrogenation. The same hydrocarbon was detected in the products of the thermolysis of 1-hydroxy[1]diadamantane for up to about 6 h. Upon treatment in cumene at 250 °C for 6.5 h it gave an approximately 3:1 mixture of **4**(2,6) and **3**.

Thermal fragmentation of 1-acetoxy[1]diadamantane, 2-AcO

1-Acetoxy[1]diadamantane, **2-AcO**, was readily obtained by acetylation of **1** or **2-OH**. The thermolysis of small samples,

† Details of the 500 MHz NMR study, with COSY and heteronuclear correlation plots, NOE experiments (Figs. 1S–6S) and a table of chemical shifts (Table 1S), are available as a supplementary publication (Supp. Pub. no. 57133 [14 pp.]). For details of the deposition scheme, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1.



1

2 – X

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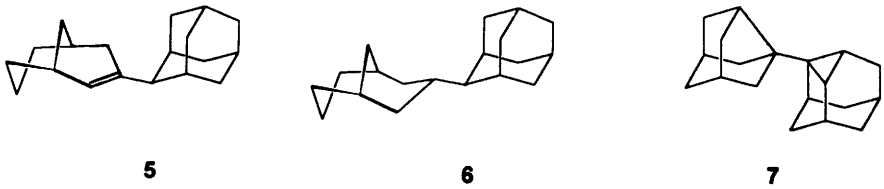

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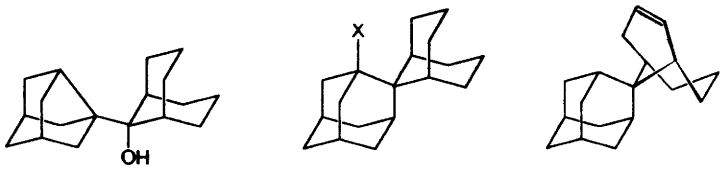


8 9 – X 10

sealed in ampoules under vacuum without solvent, gave dienes much more readily than the alcohol, the reaction being virtually complete after 1 h at 250 °C. Again the kinetic products are **3** and **7**, but these are rapidly replaced by a mixture of **3** and **4** (both isomers) in much the same final ratio (1:2.4:0.25) as for the alcohol. Minor amounts of what appear to be rearranged, stable acetates were detected. When the reaction was run in cumene the minor and major products were diene **3** and alcohol **2-OH**, respectively.

Synthesis and reactivity of 1-hydroxyspiro[adamantane-2,9′-bicyclo[3.3.1]nonane], 9-OH

The synthesis of 1-hydroxyspiro[adamantane-2,9′-bicyclo-[3.3.1]nonane], **9-OH**, from 9-(3-noradamantyl)bicyclo[3.3.1]-nonan-9-ol, **8**, resulted partly in an unsaturated material, containing a single double bond. The same material was obtained by refluxing alcohol **9-OH** in aqueous acetone containing perchloric acid. ^{13}C and ^{1}H NMR (JMOD, XHCORR and COSY) spectra identify this product as spiro[adamantane-2,9′-bicyclo[3.3.1]non-2′-ene], **10**. Pd/C-catalysed hydrogenation of this olefin gave the same alkane, **9-H**, as was obtained by TFA/TES deoxygenation [14] of the alcohol.

Discussion

Fragmentation of 1-hydroxy- and 1-acetoxy[1]diadamantanes

The first step in the reaction of 2-(3-noradamantyl)adamantan-2-ol must be the formation of a tertiary carbonium ion, the 2-(3-noradamantyl)-2-adamantyl cation, **11**. Reaction of **11** could involve fragmentation [scission of the C(3)–C(7) bond] to form cation **12**, followed by proton elimination to give **3**, as shown in Scheme 1.‡

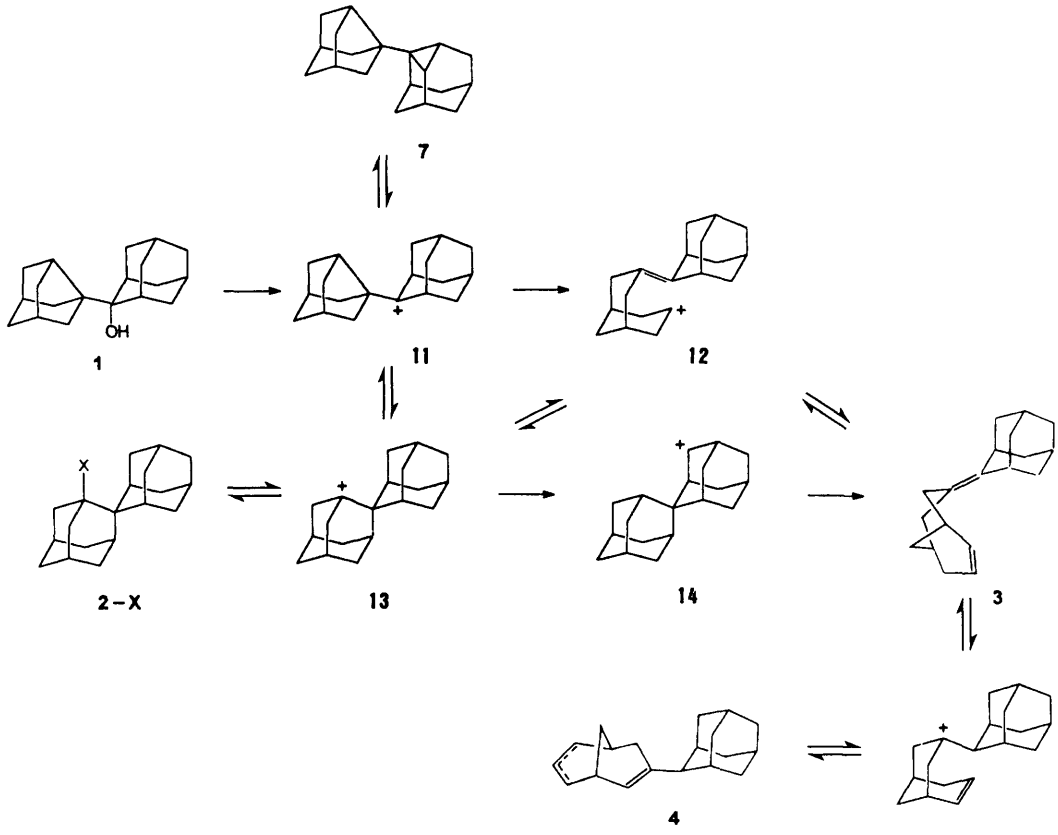
‡ For the sake of simplicity and visual continuity, in the Scheme the skeleton structure of [1]diadamantane has been used throughout (except for **1**), and most species have been oriented so that a complete adamantane group appears on the upper right-hand side. It is obvious, however, that trigonal carbon atoms will be planar and that some of the bicyclo[3.3.1]nonane derivatives will prefer a chair–boat conformation to the chair–chair form depicted.

Preliminary attempts to study the kinetics of this reaction indicate, however, that the initial alcohol, **1**, is largely converted in the first instance into the more stable 1-hydroxy[1]diadamantane, **2-OH**, which subsequently ring-opens to give the observed product, *i.e.* cation **11** rearranges to the 1-[1]diadamantyl cation, **13**, rather than fragmenting directly.

Several schemes can be written to explain the reaction of the 1-[1]diadamantyl cation, **13**. For example, scission of the C(2)–C(3) bond would lead to the same cation, **12**, as obtained by opening of **11**. An alternative, which is more closely analogous to previous work,[6,7] requires 1,4-hydrogen transfer [15] across the spiro linkage to form a secondary cation, **14**, followed by the appropriate changes in bonding to give diene **3**. Inspection of a molecular mechanics model (MM2[16] with UNICAT 4[17] carbocation parameters) of the 1-[1]diadamantyl carbocation, **13**, indicates that two of the methylene hydrogens on the non-substituted adamantane moiety (*i.e.* that which does not bear the positive charge) are approximately 2.7 Å from the cationic centre. This distance is of the same order of magnitude as those calculated on the basis of a rather more simple model for 1,3 shifts in the solvolysis of cyclohexyl tosylates.[18]

Fragmentation of cation **13** to **3** by loss of a proton from a methylene group adjacent to the cationic centre, concerted with rupture of the C(1)–C(2) bond and formation of a C(2)–C(3) double bond, raises the problem of orbital alignment, as does concerted fragmentation of **11** to the same diene.

The finding of 2-(3-noradamantyl)-2,4-dehydroadamantane, **7**, among the products in the early stages of alcohol or acetate thermolysis is somewhat surprising. This is the material which would be expected if the dehydration of alcohol **1** by thermolysis proceeded as does that of other 2-(*tert*-alkyl)adamantan-2-ols.[1] That it is formed in the thermolysis of **2-OH** or **2-OAc** indicates that the rearrangement of the 2-(3-noradamantyl)-2-adamantyl cation, **11**, to the 1-[1]diadamantyl cation, **13**, is reversible and that the rate of proton loss from one of the four methylene groups close to the cationic centre in **11** is comparable to that of fragmentation of **13** to the initial diene, **3**. Hydrocarbon **7**, however, has a



Scheme 1

strain energy (MM2) of 60.9 kcal mol^{+},§ much greater than those of the isomeric dienes (see below). Consequently, in the long run thermodynamics outweighs kinetic considerations, and **7** disappears from the product mixture as the reaction proceeds.

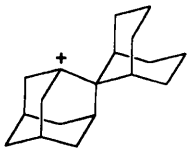
Under conditions of alcohol dehydration (or acetate thermolysis) diene **3** and the cyclopropane derivative **7** rearrange predominantly to one isomer of **4**, a 3-(2-adamantyl)bicyclo[3.3.1]nonadiene, with the minor isomer even less abundant at equilibrium than diene **3** [**3**:**4**(major):**4**(minor) = *ca.* 1:2.4:0.25]. Because of the paucity of NMR data, particularly of ^{13}C, in the literature on bicyclo[3.3.1]nonadienes[19] a fairly extensive study was necessary to establish that the major product was the 2,6-diene. Most previous work has been performed on bicyclo[3.3.1]nona-2,6-diene, but this could be a consequence of its accessibility[20] rather than its stability. An 'inseparable mixture' of 2,6- and 2,7-dienes in a ratio of 45:55 was obtained by treating the tosylhydrazone of bicyclo[3.3.1]non-2-en-7-one with *n*-butyllithium.[21] More pertinent perhaps is the report[22] that the acid-catalysed dehydration of 3-hydroxy-3-methylbicyclo[3.3.1]non-6-enes gives a 3:1 mixture of the 3-methylbicyclo[3.3.1]nona-2,6- and -2,7-dienes, consistent with our finding that the major product is the 2,6-isomer.

Molecular mechanics calculations suggest that **3** is slightly less stable than the other dienes, the MM2 strain energies of **3**, **4**(2,6) and **4**(2,7) being 25.1, 23.7 and 23.7 kcal mol^{-1}, respectively. Under our conditions the **4**(2,6)/**3** equilibrium constant is about 2.5, in fair agreement with the value (at 280 °C) of 3.5 calculated from the strain energy difference, but the very low yield of the 2,7-isomer of **4** appears anomalous. According to semi-empirical quantum mechanical (AM1) calculations[23] (which, unlike MM2, take into account interactions between the double bonds explicitly) the 3-methyl-2,7-diene is about 1.1 kcal mol^{-1} less stable than the 2,6-isomer, a difference not perceived by MM2 but in qualitative accord with the dehydration result. However, the *exo*-methylene derivative is calculated to be even less stable (3.6 kcal mol^{-1}). Calculations on the adamantane derivatives suggest that **3** is the most stable with **4**(2,6) and **4**(2,7) 1.5 and 1.9 kcal mol^{-1} less stable, respectively. This result is not satisfactory either but, given the limited precision of these calculations, the small energy differences involved and the fact that our experiments are performed at high temperature, this is perhaps not altogether surprising.

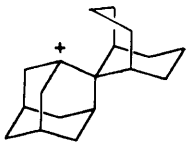
Hydrogenation of **3** gives in the first instance a bicyclo[3.3.1]non-2-ene, **5**, with the double bond adjacent to the 3-(2-adamantyl) substituent. Clearly, the least hindered bond is hydrogenated first and the other migrates to give a more stable isomer. The use of both Pd/C as catalyst and ethanol as solvent favours migration.[24] Complete hydrogenation of the equilibrated diene mixture gives exclusively *endo*-3-(2-adamantyl)bicyclo[3.3.1]nonane, **6**, the ^{13}C NMR shift of 29.1 ppm for C(9) being consistent with a chair–boat conformation.[12] Molecular mechanics calculations give strain energies (MM2) of 26.4 and 28.9 kcal mol^{-1} for the chair–chair *exo* and chair–boat *endo* isomers, respectively. If we assume that hydrogenation of the intermediate olefin involves *cis* addition to the least hindered side of the molecule,[24] then the preferential formation of the less stable, *endo* isomer indicates that the *exo* face is the more accessible.

Acetate thermolysis closely follows the pattern of that of 1-hydroxy[1]diadamantane, **2-OH**, except that reaction of **2-AcO** is substantially faster at a lower temperature. The kinetic product is again a mixture of diene **3** and **7**, and equilibration leads to a very similar mixture of the three isomeric dienes. Considered as a means of opening one of the adamantyl systems, thermolysis of the acetate is much more effective than that of the alcohol, no doubt because C–O cleavage is easier; moreover, equilibration is faster in the presence of acetic acid. An unusual aspect of acetate thermolysis is that in cumene acyl–

§ 1 cal = 4.184 J.



15 chair – chair



15 chair – boat

oxygen fission appears to compete with alkyl–oxygen fission. This phenomenon was not investigated further. At 250 °C the neat acetate gives small amounts of two apparently stable acetates. In this respect acetate decomposition may slightly resemble that of the halides discussed in the accompanying paper.[9]

Elimination from spiro[adamantane-2,9′-bicyclo[3.3.1]nonane] derivatives

At first sight, the observation that the 1-hydroxyspiro[adamantane-2,9′-bicyclo[3.3.1]nonane], **9-OH**, undergoes very ready elimination with formation of a double bond between carbons (2′) and (3′) appears to support the 1,4-hydride shift mechanism of Scheme 1. This would convert the tertiary carbocation into a secondary carbocation, the relevant C^+–H distances in the tertiary carbocation **15** being again 2.7 Å, and could be followed by or concerted with proton abstraction from the 3′-position. Such an elimination is not possible in the 4-[1]diadamantyl cation, **14**, since it would lead to an anti-Bredt olefin; the alternatives are reaction with solvent to give diadamantane or fragmentation to, in the first instance, the major diene, **3**, that obtained initially in alcohol or acetate thermolysis.

However, further consideration of the 1-spiro[adamantyl-2,9′-bicyclo[3.3.1]nonane] cation, **15**, suggests that a more likely route involves the chair–boat conformation. Though this conformation is not a stationary point on the energy profile of the alkane or the alcohol, the cation has a chair–boat energy minimum only 2.5 kcal mol^{-1} more strained than the chair–chair cation, and in this conformation one of the 3′-hydrogens is only 2.42 Å from the cationic centre. It is therefore much more likely that elimination from **15** involves not a 1,4-shift but a 1,5-shift, followed by proton loss. In acyclic systems and medium rings 1,5-shifts are known to be easier than 1,4-shifts.[25] Labelling experiments would have to be performed in order to establish the relative importance of 1,4- and 1,5-shifts in the spiro[adamantane-2,9′-bicyclo[3.3.1]nonane] system.

Conclusions

Thermolysis of the (3-noradamantyl)adamantan-2-ol or its rearrangement product, 1-hydroxy[1]diadamantane, in cumene leads to mixtures of 2-(3-noradamantyl)-2,4-dehydroadamantane and various dienes, of which one predominates at low conversion and another at equilibrium. Reaction of neat 1-acetoxy[1]diadamantane under somewhat milder conditions leads to similar mixtures, while in cumene the major product is the parent alcohol. The intermediate 1-[1]diadamantyl cation could rearrange in part to the 4-[1]diadamantyl cation *via* a 1,4-hydride shift from one adamantane moiety to the other, but results on 9-(3-noradamantyl)bicyclo[3.3.1]nonan-9-ol and the corresponding spiro alcohol are best interpreted in terms of a 1,5-hydride shift, which is impossible in the [1]diadamantane system.

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 Me_4Si (δ_H = 0.00 ppm for ^1H) or to the solvent (δ_C = 77.0 ppm for ^{13}C). Details of the NMR conditions for the study of **4**(2,6) are given in the Supplementary Publication. Melting points were determined in capillary glass tubes on a Mettler FP5 instrument with a heating rate of 3 °C min^{-1}. Gas chromatography was performed either on a packed SE30 column (30 cm) or, for coupled GC/MS [Finnigan MAT ITD 800B Ion Trap Detector with chemical ionization (isobutane)], on a CP-Sil 5 capillary column (25 m).

3-Noradamantylcarboxylic acid. Synthesized from adamantan-2-one by the method of Black and Gill.[26]

3-Bromonoradamantane. By the modified Hunsdiecker method of Baker, Holtz and Stock.[27] To 3-noradamantylcarboxylic acid (4.0 g, 24 mmol) and mercuric oxide (4 g, 18 mmol) mechanically stirred in dibromomethane (35 cm^3) at 85–90 °C was added slowly (*ca.* 0.5 h) a solution of bromine (1.2 cm^3, 23 mmol) in dibromomethane (15 cm^3). The mixture was then heated for a further hour, cooled and filtered. The solvent was evaporated and the residue chromatographed on alumina in light petroleum (bp 35–60 °C). Solvent was evaporated from the first fractions which contained virtually pure bromide (by GC) to give a mushy solid (3.5 g, 71%) which was used without further purification: δ_C 66.2 (C_q), 55.3 (2 CH_2), 48.6 (CH), 43.3 (2 CH_2), 38.4 (2 CH) and 33.3 (CH_2).

2-(3-Noradamantyl)adamantan-2-ol, 1. Lithium sand was prepared by melting lithium metal (0.7 g, 0.1 mol) in vaseline oil under argon and stirring vigorously with a stainless steel flail while cooling. The sand was washed three times with hexane, and then sodium–dry diethyl ether (100 cm^3) was added. To the vigorously stirred dispersion at −30 °C was added slowly (*ca.* 15 min) a solution of 3-bromonoradamantane (4.0 g, 20 mmol) and adamantan-2-one (3.0 g, 20 mmol) in diethyl ether (50 cm^3). After complete addition, the temperature was allowed to rise slowly (*ca.* 1.5 h) to −10 °C and stirring was continued for 1 h with the cooling bath removed. Residual lithium was filtered off through glass wool and the reaction mixture quenched with ethanol, followed by extraction with water and hexane. The organic phase was washed with water, dried ($MgSO_4$) and the solvent evaporated. Chromatography on alumina in light petroleum–diethyl ether mixtures gave the alcohol (2.6 g, 48%): mp 177–178 °C; *m/z* (ITD) 271, 256, 255 (100%), 254, 253, 173, 151, 135, 93 and 79; δ_C 59.2 (C_q), 47.2 (2 CH_2), 44.0 (2 CH_2), 41.3 (CH), 39.6 (CH_2), 37.2 (2 CH), 35.8 (2 CH), 35.5 (CH_2), 35.2 (2 CH_2), 34.4 (2 CH_2), 27.4 (CH) and 27.0 (CH). 2,2′-Dihydroxy-2,2′-biadamantane was also isolated (1.1 g, 37%): mp 266–267 °C (lit.,[11] 267–269 °C); δ_C 79.9 (2 C_q), 39.7 (2 CH_2), 35.5 (4 CH_2), 35.2 (4 CH_2), 34.8 (4 CH), 27.2 (2 CH) and 26.9 (2 CH).

1-Hydroxy[1]diadamantane, 2-OH. Crude 2-(3-noradamantyl)adamantan-2-ol, **1** (prepared as above, prior to chromatography) was refluxed for 2 h in 0.1 M perchloric acid in 80% aq. acetone (180 cm^3 acetone, 45 cm^3 water, 2 cm^3 70% perchloric acid). On cooling, 1-hydroxy[1]diadamantane, **2-OH**, crystallized out (2.9 g, 53%); a further 0.5 g (9%) was obtained by diethyl ether extraction of the mother liquors and alumina chromatography of the residue after solvent evaporation: mp 224 °C (hexane) (lit.,[8] 224–225 °C); *m/z* (ITD) 271, 256, 255 (100%), 254, 253, 212, 176, 135, 118, 105, 95 and 79; δ_C 75.1 (C–O), 45.9 (C_q), 42.9 (2 CH_2), 40.7 (CH_2), 37.6 (CH_2), 35.0 (2 CH_2), 33.9 (CH), 33.4 (2 CH_2), 30.8 (2 CH), 30.6 (CH), 30.6 (CH_2), 27.8 (CH) and 27.2 (CH). 2,2′-Epoxy-2,2′-biadamantane was also isolated (0.9 g, 33%): mp 181–182 °C (lit.,[11] 181.5–183 °C); δ_C 73.6 (2 C_q), 37.4 (4 CH_2), 36.8 (2 CH_2), 35.1 (4 CH_2), 31.7 (4 CH) and 27.2 (4 CH).

[1]Diadamantane, 2-H. To 2-(3-noradamantyl)adamantan-2-ol, **1** (50 mg, 0.18 mmol) stirred in dichloromethane (5 cm^3) at *ca.* 5 °C was added trifluoroacetic acid (0.5 cm^3) and triethylsilane (0.2 cm^3, 1.2 mmol). After 2 h the mixture was quenched with water, washed, and the organic layer dried over $MgSO_4$. Evaporation of the solvent left a white product (46

mg, 98%): mp 254 °C (diethyl ether) (lit.,[2a,b] 252.3–255.1 °C, 249–251 °C); *m/z* (ITD) 257, 256, 255 (100%), 213, 199, 173, 135, 107, 93, 91, 81, 80 and 79; δ_C 40.7 (C_q), 39.5 (2 CH_2), 31.8 (8 CH_2), 30.2 (4 CH) and 27.6 (4 CH). The signal at 37.5 ppm attributed by Sosnowski[8] to the spiro carbon is clearly absent from our spectrum.

Thermolysis of 2-(3-noradamantyl)adamantan-2-ol, 1. 2-(3-Noradamantyl)adamantan-2-ol, **1** (0.574 g, 2 mmol) dissolved in cumene (4.5 cm^3) was sealed under vacuum in thick-walled glass ampoules and treated for 10 h at 280 °C in a silicone oil-filled thermostat. **(DANGER: Despite considerable care taken in the preparation of sealed ampoules, heating cumene solutions to 280 °C occasionally resulted in explosions.)** After cooling, the solvent was evaporated and the residue chromatographed on alumina in light petroleum–diethyl ether mixtures to give 1-hydroxy[1]diadamantane, **2-OH** (0.215 g, 38%) and a four-component hydrocarbon mixture (0.280 g, 55%): *ca.* 5, 89, 5 and 1% in order of elution. The major component was identified as 3-(adamantylidene)bicyclo[3.3.1]non-6-ene, **3**: mp 137 °C (acetone); *m/z* (ITD) 256, 255, 254 (100%), 253, 212, 176, 173, 161, 135, 119, 107, 105, 91 and 79; δ_C 140.4 (C_q), 130.5 (CH), 127.5 (CH), 121.1 (C_q), 40.6 (CH_2), 39.0 (CH_2), 38.9 (CH_2), 38.8 (CH_2), 37.4 (CH_2), 37.2 (CH_2), 33.3 (CH_2), 32.7 (CH_2), 32.5 (CH), 32.4 (CH_2), 32.2 (CH), 31.9 (CH), 29.9 (CH), 28.5 (CH) and 28.1 (CH) (Found: C, 89.8; H, 10.3. $C_{19}H_{26}$ requires C, 89.70; H, 10.30%).

Partial diene hydrogenation: 3-(2-adamantyl)bicyclo[3.3.1]-non-2-ene, 5. Reduction of a sample consisting largely of **3** (100 mg, 0.4 mmol), obtained by thermolysis of **1** in cumene, in ethanol (50 cm^3) by hydrogen (3 bar) in the presence of 10% palladium/charcoal (100 mg) for 20 min gave a mixture which upon recrystallization yielded an olefin, identified by its ^{13}C NMR spectrum as 3-(2-adamantyl)bicyclo[3.3.1]-non-2-ene, **5** (72 mg, 72%): mp 133 °C (hexane); *m/z* (ITD) 258, 257, 256, 255 (100%), 213, 173, 135, 121, 107, 93, 91, 81, 80 and 79; δ_C 140.6 (C_q), 123.8 (CH), 49.0 (CH), 39.2 (CH_2), 39.2 (CH_2), 38.0 (CH_2), 34.3 (CH_2), 34.0 (CH_2), 32.4 (CH_2), 32.3 (CH_2), 32.1 (CH_2), 30.0 (CH_2), 29.9 (CH), 29.7 (CH), 29.1 (CH), 28.2 (CH), 28.1 (CH), 27.7 (CH) and 18.6 (CH_2) (Found: C, 88.6; H, 11.1. $C_{19}H_{28}$ requires C, 88.99; H, 11.01%). The supernatant liquid from recrystallization contained the first-eluted material obtained with **3** by thermolysis of **1**. Further crystallization from hexane or acetone and reaction of olefin **5** with *m*-chloroperbenzoic acid in dichloromethane gave a very small sample of 2-(3-noradamantyl)-2,4-dehydroadamantane, **7**, about 95% pure: *m/z* (ITD) 255, 254, 253 (100%), 212, 211, 176, 173, 135, 119, 105, 93, 92, 91, 81 and 79; δ_C 51.8 (C_q), 50.9 (CH_2), 47.3 (CH_2), 46.9 (CH_2), 44.7 (CH_2), 44.4 (CH_2), 40.0 (C_q), 39.4 (CH, J_{CH} 136 Hz), 37.1 (CH, 135 Hz), 37.0 (CH, 135 Hz), 35.9 (CH, 133 Hz), 35.6 (CH_2), 34.1 (CH_2), 32.9 (CH_2), 32.7 (CH, 135 Hz), 29.3 (CH_2), 26.7 (CH, 162 Hz), 26.4 (CH, 134 Hz) and 22.9 (CH, 156 Hz); δ_H 1.1–2.3 ppm.

Thermolysis of 1-hydroxy[1]diadamantane, 2-OH. Samples of 1-hydroxy[1]diadamantane, **2-OH** (0.137 g, 0.5 mmol) dissolved in cumene (1 cm^3) were sealed under vacuum in medium thick-walled glass tubes and thermolysed at 280 °C for various times. Hydrocarbons were separated from alcohol by column chromatography on alumina; the major product was initially **3**, described above, the yield of which fell as 3-(2-adamantyl)bicyclo[3.3.1]nona-2,6- and -2,7-dienes, **4**, were formed [capillary GC/ITD revealed two components, in a final ratio of approximately 6:1 (see below)]. An NMR study (see Supplementary Publication) of a sample enriched in the major component by crystallization from hexane at −80 °C identified it is as the 2,6-isomer, denoted **4**(2,6): *m/z* (ITD) 255, 254, 253 (100%), 212, 176, 173, 161, 135, 119, 117, 107, 105, 93, 91, 81 and 79; δ_C 136.2 (C_q), 131.7 (CH), 125.1 (CH), 124.5 (CH), 49.0 (CH), 39.1 (2 CH_2), 38.0 (CH_2), 32.9 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 31.3 (CH_2), 29.4 (CH), 29.2 (CH), 28.9 (CH_2), 28.7 (CH), 28.6 (CH), 28.1 (CH) and 28.0 (CH). The minor component has: δ_C(very incomplete) 137.3 (C_q), 133.2 (CH), 125.6 (CH), 36.6 (CH_2), 34.8 (CH_2), 31.8 (CH_2) and 25.8 (CH); *m/z* (ITD) 255, 254, 253 (100%), 252, 211, 173, 163, 135, 118, 107, 105, 93, 91, 81 and 79. GC analysis of the products on a packed column gave the following results (time/h, **3**/%, **4**/%, residual **2-OH**/%): 3, 35, 2, 53; 6, 49, 5, 39; 9, 49, 18, 31; 12, 60, 26, 12; 20, 30, 70, 0. The first two samples also contained the hydrocarbon **7**. ^{13}C NMR analysis of the equilibrium mixture gave a diene composition slightly different from that indicated by the ITD response, **3**:**4**(2,6):**4**(2,7) being 1:2.5:0.28.

Thermolysis of 2-(3-noradamantyl)-2,4-dehydroadamantane, 7. A sample (*ca.* 5 mg) of a 50:50 mixture of hydrocarbon **7** and olefin **5** was dissolved in cumene (0.05 cm^3) and sealed under vacuum in a small glass ampoule. After heating for 6.5 h at 250 °C the solvent was removed and the residue taken up in $CDCl_3$. The ^{13}C NMR spectrum showed that, in addition to residual **5**, there was a roughly 3:1 mixture of **4**(2,6) (δ 140.6, 131.7, 125.1 and 124.5) and **3** (δ 130.5 and 127.5).

Diene hydrogenation: *endo*-3-(2-adamantyl)bicyclo[3.3.1]-nonane, 6. Reduction of an equilibrium mixture of **3** and **4** (100 mg, 0.4 mmol) in ethanol (50 cm^3) by hydrogen (3 bar) in the presence of 10% palladium/charcoal (0.5 g) for 24 h gave a saturated hydrocarbon (92 mg, 91%) identified by its ^{13}C NMR spectrum as **6**: mp 170 °C (hexane); *m/z* (ITD) 258, 257, 256, 201, 187, 179, 161, 149, 136, 135 (100%), 123, 122, 121, 109, 107, 93, 91, 81, 80 and 79; δ_C 51.4 (CH), 39.4 (2 CH_2), 38.4 (CH_2), 33.7 (2 CH_2), 32.0 (2 CH_2), 31.1 (2 CH_2), 29.1 (CH_2), 28.7 (2 CH), 28.1 (CH), 27.9 (CH), 27.9 (CH), 25.7 (2 CH) and 15.9 (CH_2) (Found: C, 88.3; H, 11.8. $C_{19}H_{30}$ requires C, 88.30; H, 11.70%).

1-Acetoxy[1]diadamantane, 2-AcO. Refluxing either 1-hydroxy[1]diadamantane or 2-(3-noradamantyl)adamantan-2-ol in acetic acid containing 10% of acetic anhydride for 1 h, followed by diethyl ether extraction, washing with water, drying and evaporation of the solvent, gave the acetate practically quantitatively: mp 127 °C (hexane); *m/z* (ITD) 314, 271, 256, 255 (100%), 254, 253, 173, 135, 107, 105, 95, 93, 91 and 79; δ_C 169.2 (C=O), 88.3 (C–O), 45.8 (C_q), 41.0 (CH_2), 37.0 (CH_2), 34.5 (CH), 34.4 (2 CH_2), 34.3 (2 CH_2), 33.6 (2 CH_2), 30.7 (2 CH), 30.5 (2 CH_2), 30.4 (2 CH), 27.7 (CH), 27.1 (CH) and 23.8 (CH_3) (Found: C, 80.5; H, 9.7. $C_{21}H_{30}O_2$ requires C, 80.21; H, 9.62%).

Thermolysis of 1-acetoxy[1]diadamantane, 2-AcO. Samples (30–40 mg) of **2-AcO** sealed under vacuum in *ca.* 0.2 cm^3 ampoules were thermolysed at 250 °C for times ranging from 20 min to 6 h. According to GC analysis the first sample contained **3** and **7** in a ratio of about 10:1, and the reaction was complete in about 1 h, the main product (72% of the dienes) then being **3**. The diene mixture attained the equilibrium composition [**3**:**4**(2,6):**4**(2,7) being 1:2.4:0.25 by ^{13}C NMR analysis] in less than 6 h. Small amounts (*ca.* 6% of the total) of two higher retention time, stable acetates [*m/z* (ITD) 314, 271, 256, 255 (100%), 254, 253, 173, 107, 93 and 79 and *m/z* (ITD) 313, 271, 256, 255 (100%) 254, 253, 173, 91 and 79] were detected in all samples.

Thermolysis of **2-AcO** (170 mg, 0.54 mmol) in cumene (0.5 cm^3) for 2 h at 250 °C gave a mixture of diene **3** (53 mg, 39%) and alcohol **2-OH** (86 mg, 58%).

1-Hydroxyspiro[adamantane-2,9′-bicyclo[3.3.1]nonane], 9-OH. Reaction of 3-bromonoradamantane (1.8 g, 9 mmol) and bicyclo[3.3.1]nonan-9-one (1.0 g, 7.2 mol) with finely divided lithium metal (0.4 g, 0.06 mol) under the conditions used for the synthesis of 2-(3-noradamantyl)adamantan-2-ol, **1** (above) gave **8** as a crude product, which was refluxed for 1 h in 80% aqueous acetone (100 cm^3) containing perchloric acid (70%, 1 cm^3). Diethyl ether extraction gave 0.8 g of a mixture which, by chromatography on alumina in light petroleum–diethyl ether mixtures, yielded the required alcohol, **9-OH** (0.38 g, 20%): mp 176–177 °C (hexane); *m/z* (ITD) 259, 244, 243 (100%), 242, 241,

187, 161, 135, 122, 107, 95, 81 and 79; δ_C 74.5 (C_q), 43.2 (C_q), 42.7 (2 CH_2), 37.7 (CH_2), 33.7 (CH), 30.8 (2 CH_2), 30.5 (2 CH), 30.3 (2 CH), 29.6 (2 CH_2), 28.3 (2 CH_2), 20.3 (CH_2) and 20.2 (CH_2) (Found: C, 82.7; H, 10.9%. $C_{18}H_{28}O$ requires C, 83.02; H, 10.84%). Other products included olefin **10** (see below) (0.301 g, 17%) and an epoxide (143 mg, 15%) derived from the diol obtained by coupling of bicyclo[3.3.1]nonyl ketyl radicals: mp 167–168 °C (hexane); *m/z* (ITD) 261, 243, 217, 179, 161, 140, 139 (100%), 123, 122, 121, 110, 109, 93 and 79; δ_C 72.6 (2 C_q), 31.8 (4 CH_2), 31.8 (4 CH), 29.5 (4 CH_2), 21.4 (2 CH_2) and 21.3 (2 CH_2) (Found: C, 83.2; H, 10.8%. $C_{18}H_{28}O$ requires C, 83.02; H, 10.84%).

Spiro[adamantane-2,9′-bicyclo[3.3.1]nonane], 9-H. To a stirred solution of 1-hydroxyspiro[adamantane-2,9′-bicyclo-[3.3.1]nonane], **9-OH** (130 mg, 0.5 mmol) in dichloromethane (10 cm^3) at room temperature was added triethylsilane (0.25 cm^3, 1.6 mmol), followed by the dropwise addition of trifluoroacetic acid (1 cm^3). After 0.5 h the reaction mixture was quenched with water and hexane added; the organic layer was washed with water and dried. Evaporation of the solvent left a white solid slightly contaminated with organosilicon derivatives. Chromatography on alumina in light petroleum gave the pure material (110 mg, 90%): mp 188 °C; *m/z* (ITD) 244, 243 (100%), 202, 201, 187, 161, 135, 121, 108, 107, 105, 95, 93, 92, 91, 81, 80 and 79; δ_C 39.5 (CH_2), 37.6 (C_q), 31.7 (4 CH_2), 30.1 (2 CH), 29.9 (2 CH), 27.6 (2 CH), 26.2 (4 CH_2) and 21.0 (2 CH_2) (Found: C, 88.2; H, 11.7. $C_{18}H_{28}$ requires C, 88.45; H, 11.55%).

Spiro[adamantane-2,9′-bicyclo[3.3.1]non-2′-ene], 10. Refluxing alcohol **9-OH** (40 mg, 0.15 mmol) for 5 h in 75% aqueous acetone (40 cm^3) containing perchloric acid (70%, 1 cm^3) gave, after chromatography on alumina in light petroleum, olefin **10** (27 mg, 73%): mp 156–157 °C (hexane); *m/z* (ITD) 243, 242, 241 (100%), 240, 213, 185, 173, 161, 149, 135, 121, 105, 93 and 79; δ_C 128.9 (CH), 128.0 (CH), 39.4 (CH_2), 38.0 (C_q), 33.8 (CH), 32.8 (CH_2), 32.3 (CH_2), 32.0 (CH_2), 32.0 (CH_2), 31.3 (CH), 30.4 (CH_2), 29.9 (CH), 29.5 (CH), 27.7 (CH), 27.7 (CH), 27.7 (CH_2), 22.2 (CH_2) and 16.6 (CH_2); δ_H 1.1–2.4 (br m, 20 H), 2.1–2.4 (br m, 3 H), 2.72 (br d, 1 H), 5.50 (m, 1 H) and 5.82 (m, 1 H) (Found: C, 88.8; H, 10.9%. $C_{18}H_{26}$ requires C, 89.19; H, 10.81%).

Reduction of **10** in ethanol by hydrogen (3 bar) in the presence of 10% Pd/C for 8 h gave almost quantitatively a saturated hydrocarbon, identified by its ^{13}C NMR spectrum as **9-H**.

Molecular mechanics calculations

Strain energies and geometries of hydrocarbons were calculated with Allinger's MM2(85)[16] force field, using block matrix minimization. Steric energies and geometries of carbocations are based on the MM2 force field with the addition of Müller's UNICAT 4[17] parameter set.

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