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

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Tertiary 1-halospiro[adamantane-2,2′-adamantane] derivatives (1-halo[1]diadamantanes) have been synthesised by reaction of the 1-[1]diadamantyl cation with appropriate nucleophiles. Thermolysis of 1-chloro- or 1-bromo-[1]diadamantane, but not the 1-fluoro derivative, gives the corresponding secondary 4-halo derivative in good yield. By ^{1}H and ^{13}C NMR spectroscopy and by X-ray crystallography it has been established that the 4-bromo[1]diadamantane isolated is the *anti* isomer, with the Br–C–C–C_{spiro} torsion angle close to 170°, this being the less strained of the two possible 4-substituted isomers, according to molecular mechanics calculations. Possible mechanisms for the rearrangement are discussed.

Inspection of work on polycyclic hydrocarbons reveals that the vast majority of substitution products reported are tertiary derivatives. For example, in Fort's 1976 book on adamantanes,[1] bridgehead derivatives occupy 14 pages of Tables while secondary barely fill two. Despite the fact that bridgehead carbocations are strained, witnessed by their relatively slow formation in solvolysis reactions,[2] substitution *via* carbocationic processes catalysed by Lewis acids[3] is a relatively efficient means of replacing tertiary hydrogen by halogen, for example. Radical substitution processes are less selective and generally unsuitable for synthesis. However, free radical hydroxylation of adamantane[4] gives 1- and 2-adamantanols, the latter of which can be retrieved by oxidation to the ketone, a very useful precursor for secondary adamantyl derivatives. Nevertheless, adamantan-2-one is much more readily obtained by treating adamantane with concentrated sulfuric acid.[5]

Equilibration of adamantyl chlorides by means of Lewis acids in Lewis acid solvents[6] gives mixtures with 1:2 ratios of 10 to 16, corresponding to an energy difference of about 2 kcal mol^{-1}, while the strain energy difference calculated by molecular mechanics (MM2)[6] is only 0.8 kcal mol^{-1}.† Experimentally determined differences in the heats of formation of 1- and 2-substituted adamantanes[7] are 2.8, 3.6 and 4.4 kcal mol^{-1} for OH, Me and CO_2H, respectively, these differences being also underestimated by 1–2 kcal mol^{-1} by molecular mechanics calculations. Inspection of other well known polycyclic systems (bicyclo[2.2.2]octane, twistane, homoadamantane, diamantane, [2]diadamantane, *etc.*) suggests that tertiary derivatives are almost systematically less strained than their secondary counterparts. However, calculations on spiro[adamantane-2,2′-adamantane][8] (more usually referred to as [1]diadamantane[9]) indicate that the reported 1-substituted tertiary derivatives should be less stable than any of the potential secondary derivatives, this essentially because of the interaction of the 1-substituent with the closest methylene hydrogens of the non-substituted adamantyl unit. This interaction makes the solvolysis rate for 1-chloro[1]diadamantane, **2-Cl**, one of the highest recorded for bridgehead chlorides.[10]

† 1 cal = 4.184 J.

Other bridgehead-substituted derivatives have been obtained by bromination of the parent hydrocarbon, one to four bromine atoms entering at the tertiary positions remote from the spiro linkage,[11] but no substitution at methylene carbons has been reported. We report here new aspects of the chemistry of [1]diadamantane, including the first syntheses of derivatives, other than the ketone,[8a] substituted at one of the secondary positions.

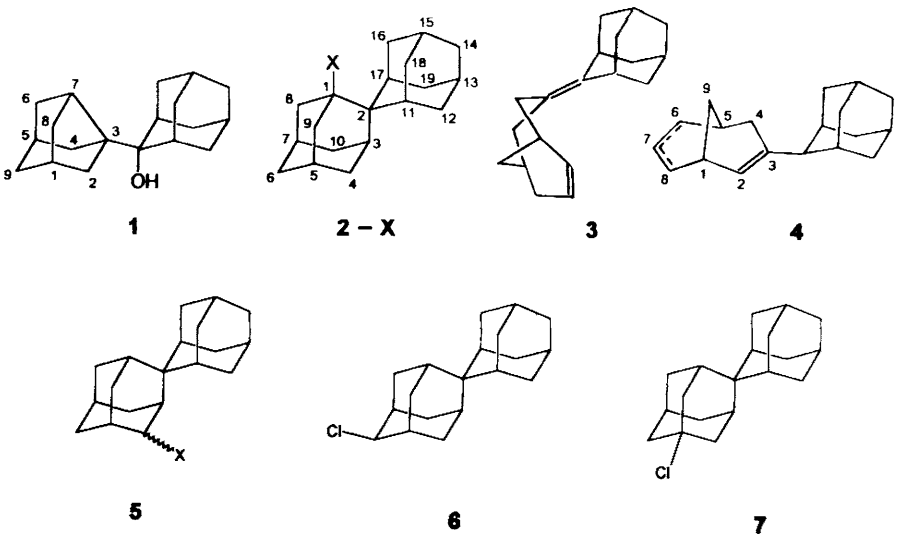
Results

Thermal rearrangement and fragmentation of 1-halo[1]-diadamantanes

***(i)* 1-Chloro[1]diadamantane, 2-Cl.** Reaction of 2-(3-noradamantyl)adamantan-2-ol, **1**, or 1-hydroxy[1]diadamantane, **2-OH**, with thionyl chloride at room temperature afforded 1-chloro[1]diadamantane, **2-Cl**, in quantitative yield. Previous work[10] has shown that the product obtained in this way is analytically pure, but it must be handled rapidly or in a dry atmosphere to avoid hydrolysis. In preliminary experiments, not reported in detail here, thermolysis of small samples of the neat chloride in evacuated ampoules (1–2 mg in 0.2 cm^3 ampoules) at 200–275 °C led to several dienes, the most important at low temperature being **3**, while at high temperature **4** predominated. These products are discussed in more detail in the preceding paper.[12] At higher temperatures new chlorides were also formed, one being particularly important. The reaction could be diverted almost completely towards the principal chloride by using somewhat larger (35–40 mg) samples in the same ampoules. After thermolysis for 5 h at 250 °C it was separated from small amounts of hydrocarbons, mainly dienes, by column chromatography.

It proved to be more convenient to conduct the thermolysis experiment in cumene; in contrast to what was observed for the acetate,[12] the result is the same (69% yield), except that the major component of the hydrocarbon fraction is now [1]diadamantane, **2-H**, rather than dienes.

The new product is a secondary chloride totally lacking in symmetry. (The accidental coincidence of two different CH_2 carbon shifts in the ^{13}C NMR spectrum makes one signal twice as great as the others.) Tributyltin hydride reduction[13] of this material or 1-chloro[1]diadamantane, **2-Cl**, gave the same



1 2 – X 3 4

5 6 7

hydrocarbon, identified as [1]diadamantane, **2-H**. The rearranged chloride can only be 4- or 6-chloro[1]diadamantane, **5-Cl** or **6**, respectively, but the latter is excluded for reasons of symmetry. Two 4-chloro[1]diadamantanes are possible, depending on the Cl–C(4)–C(3)–C(2) dihedral angle, either *anti* (*ca.* 170°) or *syn* (*ca.* 74°).‡

Molecular mechanics calculations [MM2(85)][6] indicate that both should be substantially more stable than 1-chlorodiadamantane (strain energy: 41.5 kcal mol^{-1}) with the *anti* isomer more stable than the *syn* (33.1 and 35.7 kcal mol^{-1}, respectively). The stereochemistry of the rearranged product was established by study of the corresponding bromo derivative (see below).

Various experiments were performed, with and without solvent, in an attempt to obtain information concerning the mechanism of this rearrangement, but the several chlorine-containing intermediates could not be separated adequately, even by capillary GC. In one experiment 1-chloro[1]diadamantane, **2-Cl**, was heated for 5 h in a large sealed tube with no solvent. The main product was again **5-Cl**, but it was accompanied by a 7% yield of another chloride, as well as the parent hydrocarbon. Alumina chromatography gave a fraction substantially enriched with the new chloride, and subtraction of the ^{13}C NMR spectrum of **5-Cl** from that of this fraction left the spectrum of the new product, readily identified as 5-chloro[1]diadamantane, **7**, by comparison with data for the 5-bromo derivative.[11] In another experiment the relative amounts of the various hydrocarbon and chlorine-containing products were monitored by GC/ITD against time. Significant amounts of this same chloride, detectable by virtue of the fact that its retention time is somewhat shorter than those of the other isomers, were seen in **2-Cl** samples which had been thermolysed for a very short time, as little as 15 min. Its apparent yield (based solely on the comparison of its ITD response with that of the other chlorides) decreased as the reaction proceeded.

***(ii)* 1-Bromo[1]diadamantane, 2-Br.** Treatment, under the same conditions as for **2-Cl**, of 1-bromo[1]diadamantane, obtained by reaction of 2-(3-noradamantyl)adamantan-2-ol or 1-hydroxy[1]diadamantane with oxalyl bromide in benzene, gave the analogous 4-bromo derivative, **5-Br**, in good yield (75%) after a much shorter reaction time (15 min). Again, the same result could be obtained more conveniently by working in cumeme (81% yield). Corresponding strain energies for the bromides are: 1-bromo, 44.1; *anti*-4-bromo, 33.3; *syn*-4-bromo, 36.6 kcal mol^{-1}. A complete NMR spectral investigation, including COSY, proton–proton NOE experiments and heteronuclear correlation, identified the new bromide as *anti*-4-bromo[1]diadamantane.§

***(iii)* NMR Characterization of *anti*-4-bromo[1]diadamantane, 5-Br.** Taking Duddeck's increments[15] for the effect of a 2-bromo substituent on the ^{13}C NMR shifts of adamantane, and applying these to our data for [1]diadamantane, we can calculate roughly the spectrum of the *anti*- and *syn*-4-bromo[1]diadamantanes (Table 1S).¶ Effects on the non-substituted adamantane unit are assumed to be negligible. Comparison with the experimental spectrum in $CDCl_3$ shows that, apart from C(2) and C(4) whose shifts are substantially underestimated (but which are unambiguous), all the signals expected for the *anti* isomer can be distinguished (Table 1S). The predictions for the *syn* isomer, however, account very poorly for C(2) and require for C(6) and C(14) shifts of about 40 ppm, where we have only a single carbon signal (39.1 ppm). The conclusion that our product is the *anti* isomer was confirmed by COSY-45 and heteronuclear correlation experiments, as well as by X-ray crystallography (see below).

In the spectrum shown in Fig. 1S, the proton (δ 4.77 ppm) on carbon C(4) bearing the bromine atom is clearly separated from the other protons. In the COSY experiment four cross peaks are seen for this proton: two correspond to vicinal couplings (δ 1.98 and 2.47 ppm) whereas the others result from four-bond W coupling of this proton. Theoretically, if the bromine is in the *syn* position there should be vicinal couplings with H(3) and H(5) and one W coupling with H(9a), whereas in the *anti* isomer there can be W couplings with H(6e) and H(10s). The finding that there are four cross peaks is therefore consistent with the bromine being in the *anti*-4 position. Further details concerning the attribution of the NMR spectra are given in the Supplementary Publication.

***(iv)* X-Ray crystallographic characterization of *anti*-4-bromo-[1]diadamantane, 5-Br.** A single-crystal X-ray diffraction study

‡ The different substituted [1]diadamantanes can be named according to the Cahn–Ingold–Prelog rules.[14] Depending on whether the X–C–C–C_{spiro} torsion angle is close to 180° or close to 60°, the isomer is (4*A*) or (4*S*), respectively. It is more descriptive, however, to refer to the protons or substituents at C(4) [or at other carbons adjacent to C(2)] as '*anti*' or '*syn*' (abbreviated to 'a' and 's' when used to identify hydrogens attached to numbered carbons), with respect to the spiro junction, C(2).

§ Details of the 500 MHz NMR study, with COSY and heteronuclear correlation plots (Figs. 1S–3S) and tables of chemical shifts (Tables 1S–2S) are available as a supplementary publication (Supp. Pub. no. 57135 [10 pp.]). For details of the deposition scheme, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1.

¶ Application of the Cahn–Ingold–Prelog rules[14] to the hydrogens at C(6), when C(4) bears a substituent, makes the hydrogen axial to the cyclohexane ring containing C(4) pro-*S* and the equatorial hydrogen pro-*R*. We shall denote them 'ax' for axial and 'e' for equatorial.

of **5-Br** confirmed that it was the *anti* isomer [C(2)–C(3)–C(4)–Br = −170°] and provided detailed information concerning its geometry.‖

Outstanding features are the elongation of the bonds from the spiro carbon to its neighbours (1.55, 1.57, 1.57 and 1.59 Å), the reduction of the intracyclic bond angles at this carbon (105° and 106°) and the complementary opening of the four extracyclic bond angles (mean 111.5°). On the whole there is good agreement with the results of MM2 or MM3[16] calculations, though the elongation of the bonds to the spiro carbon is seen as more uniform than it is in reality. As for the bond angles, there is slightly better agreement with MM3 than with MM2.

(*v*) 1-Fluoro[1]diadamantane, 2-F. Attempted rearrangement of the corresponding 1-fluoride, 2-F, obtained by reaction of alcohol with DAST,[17] resulted only in [1]diadamantane, **2-H**.

1-Chlorospiro[adamantane-2,9′-bicyclo[3.3.1]nonane], 8-Cl
An attempt to synthesize 1-chlorospiro[adamantane-2,9′-bicyclo[3.3.1]nonane], **8-Cl**, from the corresponding alcohol, **8-OH**, and to rearrange the crude material by thermolysis under the same conditions used for 1-chloro[1]diadamantane, **2-Cl**, resulted only in an unsaturated material, spiro[adamantane-2,9′-bicyclo[3.3.1]non-2′-ene], **9** identical with that obtained by acid-catalysed dehydration of the alcohol.[12]

Discussion

The behaviour of 1-substituted [1]diadamantanes reveals an unexpected dichotomy in that fragmentation predominates in the case of the poorer leaving groups (OH, possibly catalysed by the glass surface; OAc),[12] while better leaving groups (Cl; Br) give high yields of rearranged materials in which the elements of a strong acid (HCl or HBr) appear to have recombined with the fragmentation product to give a more stable isomer. Given the present state of our understanding of the mechanisms of these reactions, it would be premature to advance reasons for this difference in behaviour and for the somewhat anomalous position of 1-fluorodiadamantane.

Rearrangement of 1-halo[1]diadamantanes
The simplest view of the transformation of a 1-halo to a 4-halodiadamantane is to consider it as a carbocation rearrangement involving a 1,2-hydride shift, but such shifts do not occur in adamantyl cations. Nevertheless, there are many reactions which require interconversion of the 1- and 2-adamantyl cations,[1,5] and it would appear that in these cases hydride transfer is intermolecular.[1] A fragmentation–recombination mechanism was suggested[18] for the rearrangement of 2-(1-adamantyl)propan-2-ol in the Koch reaction but was found to be inconsistent with isotopic labelling and dilution studies.[19] In the present case, however, given the propensity of the [1]diadamantane system for ring opening under certain conditions,[12] the fragmentation mechanism presented in Scheme 1 is proposed** The obvious first step is the opening of the 1-[1]diadamantyl cation, **10**, to give cation **11** which then loses a proton to give diene **3** or reacts with halide ion. Isomerization of **3** leads to the 3-(2-adamantyl)bicyclo[3.3.1]-nona-2,6- and -2,7-dienes, **4** (not shown), while reaction of the intermediate carbocations with halide ion would give other unsaturated halides and **5-X**, the reaction proceeding overall in the direction of the more stable 4-halo derivative. [1]Diadamantane must be formed by hydride transfer from the solvent, cumene, to the 1-[1]diadamantyl cation. There is no provision in this Scheme for the formation of a tertiary 5-halo derivative, **7**, nor for the formation of [1]diadamantane in the absence of an obvious hydride-donor. However, when the formation of thermolysis products is followed with time it is found that **7** is present at a very early stage of the reaction and that it appears to decrease in quantity as the reaction proceeds (though it seems likely that this is an artefact due to difference in the ITD response to **7** and the other chlorine-containing materials). This suggests that an intermolecular hydride transfer mechanism, such as that shown in Scheme 2, is in competition with other rearrangement mechanisms. This Scheme adequately explains the formation of

‖ For details of the CCDC deposition scheme see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1.
** The same conventions for the representation of structures as in the preceding paper[12] have been adopted.

Table 1 Comparison of X-ray crystallographic data and values calculated by molecular mechanics for *anti*-4-bromo[1]diadamantane

	X-Ray	MM2 (85)	MM3 (89)
Bond lengths (Å)			
C(1)–C(2)	1.585	1.563	1.568
C(2)–C(3)	1.566	1.569	1.573
C(2)–C(11)	1.569	1.565	1.570
C(2)–C(17)	1.546	1.564	1.569
C(3)–C(4)	1.513	1.535	1.539
C(4)–Br	1.977	1.972	1.965
Bond angles (°)			
C(1)–C(2)–C(3)	104.8	103.6	105.2
C(11)–C(2)–C(17)	106.1	103.4	105.1
C(1)–C(2)–C(11)	110.3	112.1	111.3
C(1)–C(2)–C(17)	111.8	112.5	111.8
C(3)–C(2)–C(11)	111.4	112.9	112.1
C(3)–C(2)–C(17)	112.5	112.5	111.5
C(3)–C(4)–C(5)	111.3	109.7	110.0
Torsion angle (°)			
C(2)–C(3)–C(4)–Br	−170	−169	−171

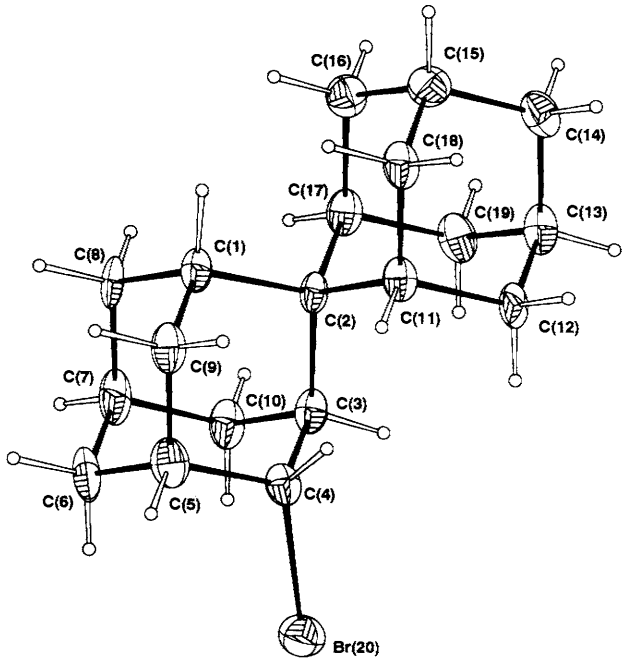
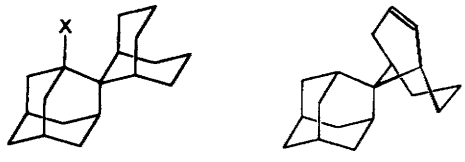
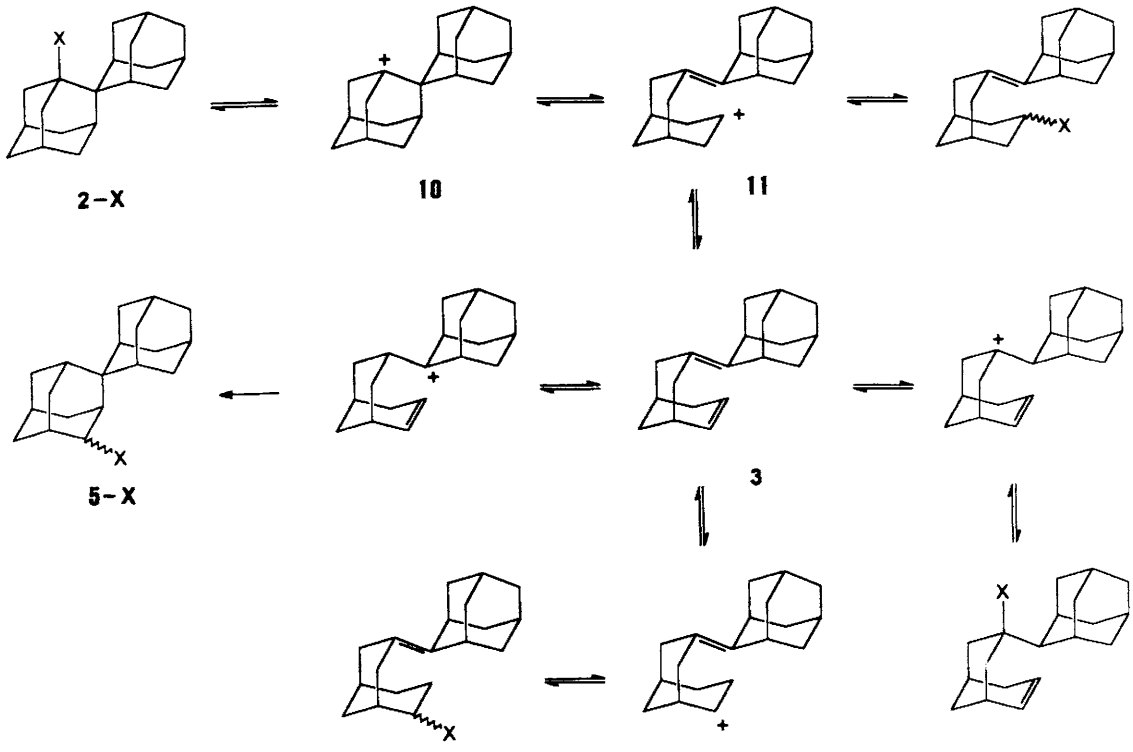


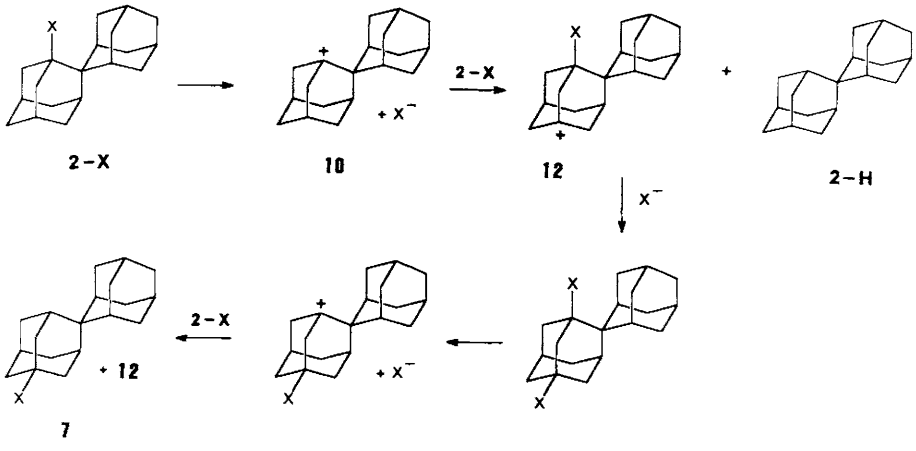
Fig. 1 CAMERON diagram of *anti*-4-bromo[1]diadamantane, **5-Br**



8-X **9**



Scheme 1

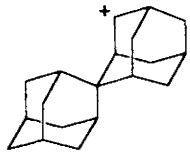


Scheme 2

[1]diadamantane, in the absence of solvent, by hydride transfer from **2-Cl** to carbocation **10**.

According to MM2 calculations (which generally underestimate the tertiary–secondary difference; see Introduction) the strain energy of the 5-chloride is 31.9 kcal mol^{-1}, *i.e.* 1.2 kcal mol^{-1} less than that of *anti* **5-Cl**. That **5-X** is the major product of 1-halo[1]diadamantane thermolysis must indicate that there is no mechanism for the conversion of this product into the thermodynamically preferred tertiary derivative. That the apparent yield of **7** stagnates suggests that, in the early stages of the reaction (less than 0.25 h), **7** is formed in competition with the other chlorine-containing intermediates, and that these latter evolve to give only **5-Cl**.

Insofar as it involves the same 1-[1]diadamantyl cation as fragmentation, the rearrangement of 1-halo[1]diadamantane could be considered to proceed in part by the 1,4-hydride shift[20] discussed in the preceding paper.[12] This shift would give a secondary carbocation, **13**, which could then react with halide at the *anti* face to give the 4-halo compound, **5-X**, or with solvent to give [1]diadamantane, **2-H** or **5-H**. This mechanism, however, does not explain the multiplicity of halides formed.



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

The observation that the analogous 1-chlorospiro[adamantane-2,9′-bicyclo[3.3.1]nonane], **8-Cl**, undergoes very ready elimination with formation of a double bond between carbons (2′) and (3′) appears to support the 1,4-shift mechanism. However, since the reaction undoubtedly proceeds through the same carbocation as acid-catalysed dehydration of the alcohol,[12] **8-OH**, the same considerations concerning the probable importance of the 1,5- rather than the 1,4-hydride shift apply in this case also.

Conclusions

1-Halo[1]diadamantanes are readily obtained by generating the 1-[1]diadamantyl carbocation from 2-(3-noradamantyl)-adamantan-2-ol or its rearrangement product, 1-hydroxy[1]-diadamantane, and reacting this with an appropriate nucleophile. Thermolysis of the 1-chloro and 1-bromo derivatives gives hydrocarbons but, under certain conditions, good yields of previously unknown 4-halo derivatives, the halogen atom being *anti* with respect to the spiro carbon. This reaction is shown to involve a number of intermediate halides, and probably proceeds largely by a fragmentation–combination mechanism. In principle, the 1-[1]diadamantyl cation could rearrange in part to the secondary 4-[1]diadamantyl cation *via* a 1,4-hydride shift from one adamantane moiety to the other, but results on the analogous spiro[adamantane-2,9′-bicyclo-[3.3.1]nonane] system, intended to pin-point this shift, do not give a clear-cut answer.

Experimental

General methods

^{13}C NMR measurements were made on a Bruker AS 200 FT instrument operating at 50 MHz. All measurements were made in $CDCl_3$ and are referenced to the solvent (δ_C = 77.0). Details of the NMR conditions used for the study of **5-Br** 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). The 1-halo[1]diadamantanes, **2-Br** and **2-Cl**, were dehydrohalogenated on the packed column; **2-F** and **2-Cl** but not **2-Br** (partial decomposition) could be chromatographed on the capillary column.

1-Chloro[1]diadamantane, 2-Cl. To 2-(3-noradamantyl)-adamantan-2-ol, **1**, or 1-hydroxy[1]diadamantane, **2-OH**, (0.574 g, 2 mmol) was added freshly distilled thionyl chloride (5 cm^3). After 15 min magnetic stirring the mixture was homogeneous. Residual thionyl chloride was removed under vacuum, leaving a white product (0.58 g, 99%) which was used without purification: *m/z* (ITD) 290, 255, 254 (85%), 213, 212, 176, 161, 135, 119, 107, 105, 93, 91, 81, 80 and 79 (100%); δ_C 78.5 (C–Cl), 48.3 (C_q), 46.3 (2 CH_2), 41.1 (CH_2), 37.1 (CH_2), 35.8 (CH), 33.8 (2 CH_2), 33.5 (2 CH_2), 31.7 (2 CH), 31.5 (2 CH), 30.3 (2 CH_2), 27.7 (CH) and 27.0 (CH).

Thermolysis of 1-chloro[1]diadamantane, 2-Cl: 4-chloro-[1]diadamantane, 5-Cl. Small samples (35–40 mg; total 140 mg, 0.48 mmol) of 1-chloro[1]diadamantane, **2-Cl**, were sealed under vacuum in 0.2 cm^3 ampoules and treated for 5–6 h at 250 °C. The residual material was chromatographed on alumina in pentane to give the secondary chloride, **5-Cl** (95 mg, 68%): mp 139.5 °C (hexane); *m/z* (ITD) 292, 291, 289, 256, 255 (100%), 253, 173, 135, 105, 93, 91, 81, 80 and 79; δ_C 65.2 (CH–Cl), 44.4 (C_q), 39.1 (CH_2), 38.1 (CH), 35.2 (CH), 32.4 (CH_2), 32.2 (CH_2), 32.1 (CH_2), 31.8 (CH_2), 31.8 (CH_2), 31.6 (CH_2), 31.5 (CH_2), 30.6 (CH), 30.3 (CH), 29.2 (CH), 27.4 (CH), 27.3 (CH), 26.7 (CH) and 24.3 (CH_2) (Found: C, 78.7; H, 9.6; Cl, 11.9. $C_{19}H_{27}Cl$ requires C, 78.45; H, 9.36; Cl, 12.19%).

More conveniently, 1-chloro[1]diadamantane, **2-Cl**, freshly prepared from 1-hydroxy[1]diadamantane, **2-OH**, (0.272 g, 1 mmol) was transferred to a medium thick-walled glass ampoule (mechanical losses are about 10%), cumene (0.5 cm^3) added and the mixture sealed under vacuum. After thermolysis at 250 °C the solvent was evaporated and the products chromatographed as above, to give 4-chloro[1]diadamantane, **5-Cl**, (0.20 g, 69%) and [1]diadamantane, **2-H** (26 mg, 10%).

1-Chloro[1]diadamantane, **2-Cl**, prepared from **2-OH** (136 mg, 0.5 mmol) was sealed under vacuum in a thick-walled glass ampoule, about 9 cm^3 in volume. After heating for 5–6 h at 250 °C, the tube was carefully opened and the contents chromatographed on alumina in light petroleum. Hydrocarbons (30 mg, 23%), mainly [1]diadamantane, **2-H**, were followed by 4-chloro[1]diadamantane (32 mg, 32%) and an approximately 2:1 mixture of 4-chloro[1]diadamantane, **5-Cl**, and another isomer (30 mg, 14 and 7%, respectively): *m/z* (ITD) 292, 291, 290, 289, 256, 255 (100%), 177, 173, 135, 107, 91 and 79. Subtraction of the ^{13}C NMR spectrum for **2-Cl**, taken under the same conditions, from that of the mixture gave the spectrum of the new chloride: δ_C 69.4 (C_q), 49.3 (CH_2), 41.9 (2 CH_2), 39.7 (C_q), 39.1 (CH_2), 34.2 (2 CH), 31.9 (2 CH_2), 31.6 (2 CH_2), 31.1 (CH), 30.4 (CH), 30.1 (CH), 29.8 (2 CH_2) and 27.4 (2 CH). This identifies the new isomer as 5-chloro[1]diadamantane, **7** (by comparison with adamantane, 1-chloroadamantane, [1]diadamantane and 5-bromo[1]diadamantane [11]).

Time dependence of products in thermolysis of 1-chloro[1]di-adamantane, 2-Cl. 1-Hydroxy[1]diadamantane, **2-OH**, (0.2 g, 0.74 mmol) was converted into the 1-chloride, **2-Cl**, as above. The product was dissolved in cumene (1 cm^3) and aliquots (*ca.* 0.05 cm^3) of the solution were transferred to small thermolysis tubes, partially degassed and sealed under vacuum. Samples were thermolysed for times ranging from 15 min to 6 h, and the products analysed by GC/ITD. Hydrocarbon products were **3**, **4** (2,6 isomer), **4** (2,7 isomer) (traces) and **2-H**. All samples contained **2-OH**. In addition to an initially broad peak representing at least three chlorine-containing compounds [**2-Cl**, **5-Cl** and other(s)] the 5-chloro derivative, **7**, was seen as a well separated peak. As calibration was not possible, the ITD output (total ion current) gives only the reaction product trend with time. The ratio of **3** to **4** fell with time (0.37 at 15 min to 0.10 at 6 h), reaching an apparent value lower than that in the thermolysis of **2-OH** or **2-AcO**.[12] Hydrocarbon **2-H** was formed increasingly as the reaction proceeded. The ratio of **7** to other chlorides fell progressively (0.26 to 0.11), reaching an apparent value higher than in preparative experiments. After 6 h the sole component of the broad chloride peak was **5-Cl**.

Reduction of chloro[1]diadamantanes. Either 1- or 4-chloro[1]diadamantane, **2-Cl** or **5-Cl**, (55 mg, 0.2 mmol) was reduced by refluxing for 2 h with tri-*n*-butyltin hydride (0.1 cm^3, 0.37 mmol) in benzene (10 cm^3) in the presence of AIBN (*ca.* 10 mg). Evaporation of the solvent under reduced pressure and washing with a small amount of cold diethyl ether gave [1]diadamantane, **2-H** (37–40 mg, 77–82%).

1-Bromo[1]diadamantane, 2-Br. Treatment of 2-(3-noradamantyl)adamantan-2-ol, **1**, or 1-hydroxy[1]diadamantane, **2-OH**, (0.272 g, 1 mmol) with excess oxalyl bromide (0.27 cm^3, 2 mmol) in benzene (5 cm^3) at room temperature for 1.5 h, followed by evaporation of the solvent and residual oxalyl bromide, gave a pale brown product which reverted rapidly to 1-hydroxy[1]diadamantane on exposure to atmospheric moisture. The crude material was used in subsequent experiments: δ_C 78.4 (C–Br), 49.6 (C_q), 48.6 (2 CH_2), 41.2 (CH_2), 37.1 (CH_2), 36.5 (CH), 33.8 (2 CH_2), 32.8 (2 CH), 32.7 (2 CH_2), 31.7 (2 CH), 30.3 (2 CH_2), 27.6 (CH) and 26.9 (CH).

Thermolysis of 1-bromo[1]diadamantane, 2-Br: 4-bromo-[1]diadamantane, 5-Br. Small samples (35–40 mg; total 0.223 g, 0.67 mmol) of 1-bromo[1]diadamantane, **2-Br**, were sealed under vacuum in 0.2 cm^3 ampoules and treated for 15 min at 250 °C. Chromatography on alumina in pentane, then 5% diethyl ether in pentane, gave a diene mixture (20 mg, 12%) and the secondary bromide, **5-Br** (167 mg, 75%): mp 141 °C (hexane); *m/z* (ITD) 335, 333, 256, 255 (100%), 173, 135, 120, 107, 91 and 79; δ_C 61.7 (C–Br), 45.2 (C_q), 39.1 (CH_2), 38.6 (CH), 35.8 (CH), 33.1 (CH_2), 32.9 (CH_2), 32.1 (CH_2), 31.8 (CH_2), 31.8 (CH_2), 31.7 (CH_2), 31.5 (CH_2), 30.9 (CH), 30.3 (CH), 29.3 (CH), 27.4 (CH), 27.3 (CH), 26.8 (CH) and 25.1 (CH_2) (Found: C, 68.2; H, 8.0. $C_{19}H_{27}Br$ requires C, 68.06; H, 8.12%).

More conveniently, 1-bromo[1]diadamantane, **2-Br**, freshly prepared from 1-hydroxy[1]diadamantane, **2-OH**, (0.272 g, 1

mmol) was transferred to a medium thick-walled glass ampoule, cumene (0.5 cm^3) added and the mixture sealed under vacuum. After thermolysis the solvent was evaporated and the products chromatographed as above to give 4-bromo[1]diadamantane, **5-Br**, (0.27 g, 81%) and [1]diadamantane, **2-H**, (19 mg, 7%).

1-Fluoro[1]diadamantane, 2-F. To 2-(3-noradamantyl)adamantan-2-ol, **1**, (0.50 g, 1.8 mmol) stirred in dichloromethane (20 cm^3) at −70 °C was added excess diethylaminosulfur trifluoride (DAST)[17] (1.1 cm^3, 8 mmol), and the mixture allowed to rise to room temperature, with stirring, overnight. The product mixture was quenched with water, and the organic phase washed and dried. Evaporation of the solvent, followed by chromatography on alumina in hexane gave **2-F**, 0.254 g (50%): mp 221 °C (pentane); *m/z* (ITD) 274, 273, 256, 255, 254 (100%), 253, 212, 173, 135, 118, 107, 105, 93, 91 and 79; δ_C 99.0 (J_{CF} 192 Hz, C–F), 46.2 (14 Hz, C_q), 40.3 (2 Hz, CH_2), 38.9 (20 Hz, 2 CH_2), 37.4 (1 Hz, CH_2), 34.8 (7 Hz, CH), 34.3 (10 Hz, 2 CH_2), 33.0 (2 CH_2), 31.3 (10 Hz, 2 CH), 30.6 (2 CH), 30.4 (1 Hz, 2 CH_2), 27.7 (CH) and 27.1 (CH) (Found: C, 83.4; H, 10.1; F, 6.8%. $C_{19}H_{27}F$ requires C, 83.16; H, 9.92; F, 6.92%).

Thermolysis of 1-fluoro[1]diadamantane, 2-F. Two samples (35 mg; total 70 mg, 0.25 mmol) were sealed in small tubes under vacuum. Treatment at 250 °C for 20 min and 1 h gave a charred mass from which [1]diadamantane, **2-H**, was isolated by chromatography (36 mg, 55%). There was no evidence for the formation of rearranged fluorides.

1-Chlorospiro[adamantane-2,9′-bicyclo[3.3.1]non-2′-ene], 8-Cl. 1-Hydroxyspiro[adamantane-2,9′-bicyclo[3.3.1]nonane], **8-OH**, (120 mg, 0.46 mmol) was stirred for 30 min with thionyl chloride (1 cm^3). Evaporation of residual thionyl chloride at reduced pressure left a pale brown solid, which was then dissolved in cumene (0.5 cm^3). The entire solution was sealed under vacuum in eight small ampoules, seven of which were heated at 250 °C for times ranging from 30 min to 8 h. Inspection of the eighth (untreated) sample revealed that it consisted largely of an olefinic material and a chloride [*m/z* (ITD) 278, 244, 243 (100%), 242, 241, 227, 187, 161, 135, 121, 108, 107, 95, 94, 93, 92, 91, 81, 80 and 79]. The treated samples contained only the olefin. Solvent was evaporated from the complete batch of samples and the residue chromatographed on alumina in light petroleum, to give olefin **9** (74 mg, 66%) identical with that reported in the accompanying paper.[12]

X-Ray crystallography

Crystal data for *anti*-4-bromo[1]diadamantane, 5-Br. $C_{19}H_{27}Br$, M = 335.3. Monoclinic, a = 7.982(1), b = 20.522(2), c = 9.193(2) Å, β = 92.61(1)°, V = 1504(1) $Å^3$ (by least squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (alt. $P2_1/c$, No. 14), Z = 4, D_x = 1.48 g cm^{-3}. Colourless prismatic crystals, μ(Mo-Kα) = 26.9 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.8 + 0.35 tan θ, graphite-monochromated Mo-Kα radiation. No decay for two standard reflections. 2908 reflections measured ($1 \leqslant \theta \leqslant 25°$), 2642 unique (merging R = 0.012), giving 1520 with $I > 3\sigma(I)$.

Structure analysis and refinement. Standard Patterson-Fourier analysis. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, and hydrogens in calculated positions with one, overall, refined isotropic thermal parameter (183 refinable parameters). Absorption correction applied (DIFABS).[21] Final R and R_w (unit weights) values are 0.043 and 0.044. Program used is the PC version of CRYSTALS[22] for refinements and CAMERON[23] for views.

Molecular mechanics calculations

Strain energies and geometries of halo compounds were calculated with Allinger's MM2 (85)[6] or MM3 (89)[16] force fields, using block matrix minimization.

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