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SHORT COMMUNICATION

1,3-ELIMINATION IN 2-(*TERT*-ALKYL)ADAMANTAN-2-OLS: AN EASY SYNTHESIS OF BRIDGEHEAD-SUBSTITUTED 2,4-DEHYDROADAMANTANES

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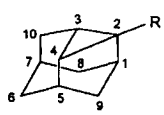
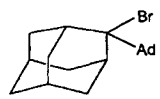
When 2-(*tert*-alkyl)adamantan-2-ols (where the substituent is bi- or tricyclic) are thermolysed or the corresponding bromide is refluxed in pyridine, an unusual 1,3-elimination occurs, leading to 2,4-dehydroadamantanes bearing the *tert*-alkyl substituent on the cyclopropane system.

1. INTRODUCTION

2,4-Dehydroadamantane (**1-H**)[1] and related compounds[2] with strained cyclopropane rings have generally been prepared by the pyrolysis of the lithium or sodium salt of the appropriate *p*-tosylhydrazone. 2,4-Dehydroadamantane has, however, also been prepared by pyrolysis of the 2-adamantyl tosylate or mesylate[3] and by Huang–Minlon reduction of 8,9-dehydroadamantan-2-one.[4] It can also be prepared from this ketone via the alcohol and the chloride.[5] It is reported to be formed (8%) in the deamination of 2-adamantylamine by the aryltriazene procedure[6] and in the catalytic hydrogenation of 2,4,6,9-tetradehydroadamantane (10%),[2a] and is one of the primary photoproducts from the irradiation of 2-adamantyl bromide or iodide in diethyl ether or methanol containing triethylamine.[7] It is a minor product (2%) in the solvolysis of a 4-substituted 2-adamantyl *p*-nitrobenzenesulphonate.[8]



1-R



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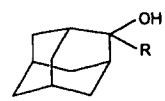

3-R

Despite all this work on the parent compound, to date only one bridgehead-substituted 2,4-dehydroadamantane has been described, the 2-methyl derivative, **1-Me**, obtained in five steps from 8,9-dehydroadamantan-2-one.[9] We now report that a very unusual 1,3-elimination leads to a remarkably simple synthesis of 2-(1-adamantyl)-2,4-dehydroadamantane (**1-Ad**), which can be extended to other bicyclic or tricyclic *tert*-alkyl substituents, such as 1-bicyclo[2.2.2]octyl or 1-norbornyl.

RESULTS AND DISCUSSION

When 1,2′-biadamantyl was synthesized by reduction of 2-(1-adamantyl)-2-bromoadamantane (**2**), the product was contaminated with a hydrocarbon of slightly shorter retention time. However, when the mixture was treated with bromine in carbon tetrachloride and the product was chromatographed on alumina in pentane, 1,2′-biadamantyl was obtained pure.[10] ^{13}C NMR on the crude material indicated that the impurity was neither of the adamantene dimers isolated by Lenoir and Firl[11] and McKervey and co-workers.[12] Refluxing the bromide in pyridine gives only the 'impurity' hydrocarbon, in 91% yield. Thermal dehydration of 2-(1-adamantyl)adamantan-2-ol (**3-Ad**) at 280 °C gives the same material, again in high yield. The ^{13}C NMR spectrum indicates two quaternary, six tertiary (relative intensities 1, 1, 1, 3, 1, 1) and six secondary carbons (relative intensities 1, 1, 1, 3, 3, 1), corresponding to $C_{20}H_{28}$, the mass of 268 Da being confirmed by mass spectrometry. Coupling constants for the two upfield CH groups are high, 164 and 154 Hz, consistent with their being part of a cyclopropane system. Signals due to the 1-adamantyl substituent are easily identified by their shifts and intensities (28·6, 3 CH; 37·3, 3 CH_2; 39·0, 3 CH_2; 43·4, 1 C_q), leaving five CH, four CH_2 and one C_q,

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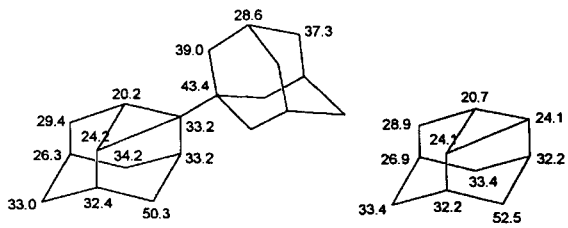
indicating that the compound is a bridgehead-substituted 2,4-dehydroadamantane. The ^{1}H NMR spectrum shows a massif stretching from 1·25 to 2·0 ppm and two broad 1H multiplets at 2·20 and 2·32 ppm. A heteronuclear correlation experiment identifies these as corresponding to CH signals at 32·4 and 33·2 ppm, respectively, of the dehydroadamantane skeleton, shown as C-1 and C-5 (not necessarily in this order) in the structure. The ^{13}C NMR spectrum closely resembles that of the parent 2,4-dehydroadamantane (**1-H**)[13] with the characteristic downfield CH_2 signal associated with the bicyclo[3.1.0]hexyl unit[13,14] (C-9) at 50·3 ppm (52·5 ppm in the parent). (Dehydroadamantanes and related compounds are frequently named and numbered with reference to the assumed parent compound. Strictly, 2,4-dehydroadamantane is tetracyclo[4.3.1.0^{2,4}.0^{3,8}]decane. Fortuitously, the downfield methylene carbon is C-9 in both numbering systems, but C-1 and C-5 will be C-1 and C-8, respectively, according to the correct notation.) The ^{13}C NMR assignments of the new derivative and of the parent compound are given for comparison.



Normally, there are two ways by which a carbocation gives molecular products, either by reaction with a nucleophile or by loss of a proton, although proton loss may be replaced by fragmentation leading to an alkene and a new, smaller carbocation. The proton or fragment to be eliminated should be on a carbon adjacent to the cationic centre and preferably in a position orthogonal to the plane of the carbocation. If the first condition is not initially satisfied, then a 1,2-sigmatropic (Wagner–Meerwein) rearrangement may displace the cationic centre so that it is. This is the situation for a *tert*-butyl attached to a charged carbon: there is initially no α-hydrogen but migration of one methyl group leaves the other two on the electron-deficient centre, which now has six αhydrogens. For this reason, *tert*-butyl groups often do not survive carbonium ion reactions.[15,16] Replacing a *tert*-butyl group by a 1-adamantyl, however, greatly reduces the rate of the corresponding rearrangement so that only under forcing conditions, such as those of the Koch reaction,[17] will the adamantyl system undergo ring expansion. There may therefore arise situations where it is kinetically and/or thermodynamically preferable to seek a proton elsewhere and for 1,3-elimination, rather than simple 1,2-elimination, to occur. This is clearly the case of the 2-(1-adamantyl)adamant-2-yl cation, for which 1,3-elimination is manifestly easier than the formation of a substituted adamantene, the anti-Bredt alkene.[11,12]

There are ample precedents for this reaction in physical chemistry. Water is eliminated from 2-adamantanol in mass spectrometry predominantly by a stereospecific 1,3-elimination from the intact skeleton (*i.e.* before α-cleavage) to give a radical cation $[C_{10}H_{14}]^{+\cdot}$ with the 2,4-dehydroadamantane structure.[18] Other 2-substituted adamantanes also undergo 1,3-elimination in mass spectrometry.[19] According to another report, possible isomeric structures of $[C_{10}H_{14}]^{+\cdot}$ from different precursors interconvert to a mixture of common ions.[20] The anodic oxidation of 2-adamantyl fluoride, but not other halides, in acetonitrile also proceeds via the 2,4-dehydroadamantyl radical cation.[21]

Analogous experiments on other 2-(*tert*-alkyl)adamantan-2-ols, where the tertiary alkyl group is 1-bicyclo[2.2.2]octyl or 1-norbornyl, indicate that they behave like the 1-adamantyl derivative, although the reaction is less clean and slower for the small 1-norbornyl substituent. Some aspects of the chemistry of 2-(3-noradamantyl)adamantan-2-ol (**3-Norad**) have recently been reinvestigated; while the major products of its thermolysis are the rearranged alcohol, 1-hydroxy[1]diadamantane, and its fragmentation products, 2-(3-noradamantyl)-2,4-dehydroadamantane (**1-Norad**) can be detected in the early stages of the reaction.[22]

EXPERIMENTAL

Alcohol synthesis. All alcohols were prepared by the one-step Barbier reaction of the appropriate 1-bromoalkane with 2-adamantanone in the presence of lithium in diethyl ether at −20 °C, following the previously described procedure.[23] Products were purified by chromatography on alumina with light petroleum–diethyl ether mixtures as eluent, followed by crystallization from hexane.

2-(1-Adamantyl)adamantan-2-ol (**3-Ad**). Yield 52%; m.p. 217–218 °C (lit.,[24] 214–215 °C; δ_C (ppm) (Bruker AC 200, $CDCl_3$), 26·9 (CH), 27·3 (CH), 29·2 (3 CH), 33·7 (2 CH), 34·9 (2 CH_2), 35·8 (2 CH_2), 37·3 (3 CH_2), 39·0 (3 CH_2), 39·5 (CH_2), 41·8 (C_q) and 77·0 (C—OH); IR (Perkin–Elmer 781, CCl_4, ν_{OH}), 3622 cm^{-1}.

2-(1-Bicyclo[2.2.2]octyl)adamantan-2-ol (**3-Oc**). Yield 44%; m.p. 174–175 °C; δ_C (ppm) ($CDCl_3$), 23·1 (CH), 26·1 (2 CH_2), 27·0 (CH), 27·3 (CH), 27·4 (2 CH_2), 34·2 (2 CH), 34·3 (2 CH_2), 35·6 (2 CH_2), 39·8 (CH_2), 39·9 (C_q) and 76·6 (in C_6D_6, C—OH); IR (CCl_4, ν_{OH}, 3623 cm^{-1}. Analysis: $C_{18}H_{28}O$ requires C 83·02, H, 10·84; found, C 82·7, H 11·0%.

2-(1-Norbornyl)adamantan-2-ol (**3-Norb**). Yield 56%; m.p. 106–107 °C; δ_C (ppm) ($CDCl_3$), 26·9 (CH), 27·2 (CH), 29·4 (2 CH_2), 31·2 (2 CH_2), 34·57 (2 CH_2), 34·64 (2 CH_2), 35·3 (2 CH), 37·8 (CH), 38·9 (CH_2), 43·6 (CH_2), 55·9 (C_q) and 76·7 (C—OH); IR (CCl_4, ν_{OH}) 3621 $^{-1}$. Analysis: $C_{17}H_{26}O$ requires C 82·87, H 10·64%; found, C 83·1, H 10·5%.

Debydrobromination: 2-(1-Adamantyl)-2,4-dehydroadamantane (**1-Ad**)2-(1-Adamantyl)adamantan-2-ol (**3-Ad**)[23] (0·1 g, 0·35 mmol) in benzene (2 cm^3) at *ca* 0 °C was stirred with oxalyl bromide (0·1 cm^3) for 1 h. The solvent and excess oxalyl bromide were removed under vacuum and the residue was refluxed with pyridine (5 cm^3) for 2 h. Chromatography on alumina yielded **1-Ad** (85 mg, 91%), m.p. 149–150 °C (hexane); *m/z* (Finnigan MAT ITD 800B) 269, 268, 267, 136, 135 (100%), 133, 107, 93, 91 and 79; δ_C (ppm) ($CDCl_3$) (carbon type, J_{CH} in Hz), 20·2 (CH, 154), 24·2 (CH, 164), 26·3 (CH, 133), 28·6 (3 CH, 132), 29·4 (CH_2, 127), 32·4 (CH, 137), 33·0 (CH_2, 129), 33·2 (CH, 137), 33·2 (C_q), 34·2 (CH_2, 124), 37·3 (3 CH_2, 127), 39·0 (3 CH_2, 127), 43·6 (C_q) and 50·3 (CH_2, 127); δ_H (ppm) ($CDCl_3$), 1·25–2·0 (several br m, 26H), 2·20 (1H, m) and 2·32 (1H, m); IR (KBr), 751, 1030, 1063, 1101, 1340, 1445, 2842, 2900, 3002 and 3020 cm^{-1}. Analysis: $C_{20}H_{28}$ requires C 89·49, H 10·51; found, C 89·5, H 10·5%.

Similar treatment of 2-(1-bicyclo[2.2.2]octyl)-adamantan-2-ol (**3-Oc**) and 2-(1-norbornyl)adamantan-2-ol (**3-Norb**) gave the corresponding substituted 2,4-dehydroadamantanes, **1-Oc** and **1-Norb**, in yields of 93 and 48%, respectively. **1-Oc**: m.p. 89 °C (hexane); *m/z* 243, 242 (100%), 241, 213, 199, 185, 135, 131, 117, 109, 105, 91, 81 and 79; δ_C (ppm) ($CDCl_3$), 21.0 (CH, J_{CH} = 155 Hz), 24·7 (CH, 134), 25·1 (CH, 169), 26·1 (3 CH_2), 26·2 (CH, 130), 27·6 (3 CH_2), 29·3 (CH_2), 31·5 (C_q), 32·5 (CH, 135), 33·0 (CH_2), 34·0 (CH_2), 34·0 (CH, 133), 42·0 (C_q) and 50·2 (CH_2); δ_H (ppm) ($CDCl_3$), 1·2–2·4 (several br m, 24H), 2·19 (m, 1H), 2·28 (m, 1H); IR (KBr), 758, 806, 1068, 1260, 1330, 1338, 1450, 2845, 2920, 3005 and 3018 cm^{-1}. Analysis: $C_{18}H_{26}$ requires C 89·19; H 10·81; found C 88·8, H 10·9%. **1-Norb**: oil, *ca* 96% pure containing inseparable impurity; *m/z* 229, 228 (100%), 227, 199, 185, 171, 157, 145, 143, 131, 129, 117, 105, 95, 93, 91, 81 and 79; δ_C (ppm) ($CDCl_3$), 24·3 (CH, J_{CH} = 155 Hz), 26·4 (CH, 132), 27·1 (CH, 164), 29·3 (CH_2), 30·7 (CH_2), 30·7 (CH_2), 32·6 (CH_2), 32·8 (CH, 134), 32·9 (CH_2), 33·0 (CH_2), 33·7 (CH_2), 35·4 (CH, 134), 36·3 (CH, 140), 38·5 (C_q), 39·6 (CH_2), 50·4 (CH_2) and 50·6 (C_q); δ_H (ppm) ($CDCl_3$) 1·2–1·9 (several br m, 22H), 2·09 (m, 1H), 2·21 (m, 1H); IR (KBr), 1026, 1067, 1099, 1323, 1341, 1454, 2850, 2862, 2940, 2999 and 3010 cm^{-1}.

Dehydration: thermolysis of 2-(Adamantyl)-adamantan-2-ol (**3-Ad**). 2-(1-Adamantyl)adamantan-2-ol (0·286 g, 1 mmol) was sealed under vacuum in a thick-walled tube and heated at 280 °C for 3 h. After cooling, the tube was carefully opened and the products were separated by chromatography on alumina to give residual alcohol (15 mg, 5%) and 2-(1-adamantyl)-2,4-dehydroadamantane (**1-Ad**) (0·243 g, 91%).

In the same way, 2-(1-bicyclo[2.2.2]octyl)-2,4-dehydroadamantane (**1-Oc**) and 2-(1-norbornyl)-2,4-dehydroadamantane (**1-Norb**) were obtained from the corresponding alcohols in yields of 94% (277 °C, 5 h) and 46% (285 °C, 5 h), respectively.

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