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AN INTRAMOLECULAR 1,3-HYDRIDE SHIFT IN THE ADAMANTANE NUCLEUS

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Within the adamantane nucleus a 1,3-hydride shift[1] would most likely occur between the 2 and 4 position because of favourable stereochemical requirements. In this paper we want to report substantial evidence for a 1,3-hydride shift in biadamantylsystems.[2]

When glycol I[3], epoxide II[3] or spiroketone III[3] was treated with 50 vol% sulphuric acid at about 140° (heterogeneous reaction conditions), two products were isolated, one of which the spiroketone III. The other compound was identified as 4-(2'-adamantyl)adamantan-2-one (IV).[4] (See fig. 1).

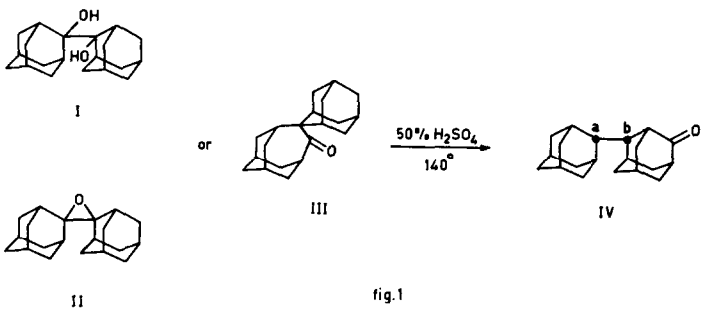


fig.1

This result may be explained by the following mechanism:

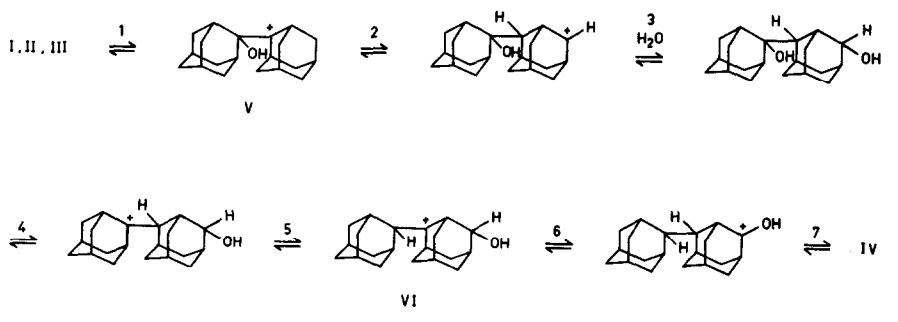
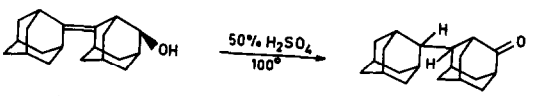


fig. 2

The nature of steps 2 and 6 is not clear however. An inter- as well as intramolecular process might occur here. Although an intermolecular pathway seems the most attractive of both possibilities[5], the total absence of disproportionation products and the seemingly unexplainable reactivity of the methylene hydrogens in V, forced us to have a closer look at the alternative intramolecular process of a 1,3-hydride shift.

Using trifluoroacetic acid as cosolvent, the reaction was run under homogeneous conditions with all mentioned substrates at extreme dilution (10^{-4} and 10^{-6}M). We again found III and IV as reaction products. This is in sharp contrast with the results obtained in the isomerization studies of the 1- and 2-adamantylcation, where at $4x10^{-4}$M no isomerization was observed, indicating an intermolecular hydride exchange.[6]

When 4e-hydroxyadamantylideneadamantane (VII)[7] was treated with 50 vol% sulphuric acid, IV was isolated as the sole product (see fig. 3). Note that VII is in fact the logical precursor of the carbonium ion VI in fig. 2. Optimal conditions were obtained at slightly lower temperature than the original. Again when the reaction was carried out with trifluoroacetic acid as cosolvent under strictly homogeneous conditions at 10^{-4} and 10^{-6}M this result was obtained.

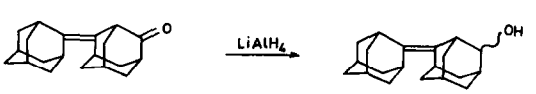


VII IV

fig.3

Since dilution studies in the absence of exact kinetic data are no definite proof of the intra- or intermolecular nature of a transformation, we focused our attention on the stereochemical requirements of the conversion of VII.

In the absence of epimerization at the hydroxylated carbon of VII only the equatorial 4-hydroxyadamantylideneadamantane is supposed to react, the axial one remaining unchanged. To prove this a mixture of both isomers was prepared by $LiAlH_4$ reduction of the ketone VIII (see fig. 4).[7]



VIII

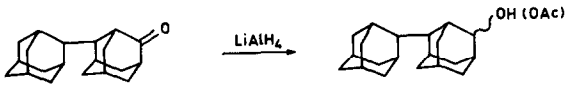
fig.4

When this mixture was treated with 50 vol% sulphuric acid under the same conditions as before, the ketone IV was formed and indeed the 4a-hydroxyadamantylideneadamantane remained unchanged. Since it is highly unlikely that the 4-axial hydrogen would undergo homoallylic activation, this experiment furnishes additional proof of the intramolecular nature of the rearrangement process.

If an intramolecular rearrangement to give IV is operative, certain stereochemical restrictions must be observed. One of these is that the ketone IV will have a configuration in which the adamantane substituent is in an equatorial position with regard to the carbonyl containing ring

The actual stereochemistry of IV was determined as follows. First of all, the sharp melting range ($0,3^{\circ}$) is not inconsistent with a single species. This was further substantiated by a failure of separation into components on highly selective GC columns and finally by an analysis of CMR and $Eu(DPM)_3$ extended PMR spectra (see below).

The choice between axial or equatorial was made by chemical means. Reduction of IV with $LiAlH_4$ gave a mixture of two alcohols as demonstrated by the melting range ($142-184^{\circ}$) (see fig. 5). Decisive proof for the duality of this product was obtained after conversion to acetates. The GC of this mixture gave two peaks.



IV

fig.5

These results are only compatible with an equatorial position. $LiAlH_4$ reduction of an axial isomer is supposed to give only one reduction product c.q. acetate as a consequence of steric approach control. This is supported by results obtained by McKervey in the reduction of 4,4-dimethyladamantanone.[8]

Final proof for the intramolecular nature of step 6 (fig. 2) was found in a selective deuteration reaction. VIII (see fig. 4) was reduced with $LiAlD_4$ to a mixture of deuteroalcohols, from which the equatorial isomer IX was separated by fractional crystallization (see fig. 6). This compound was converted into the deuterated ketone IV under the same conditions as employed in the conversion of alcohol VII to IV. The nature of the rearrangement process was expected to give a different deuterium distribution around the central bond.

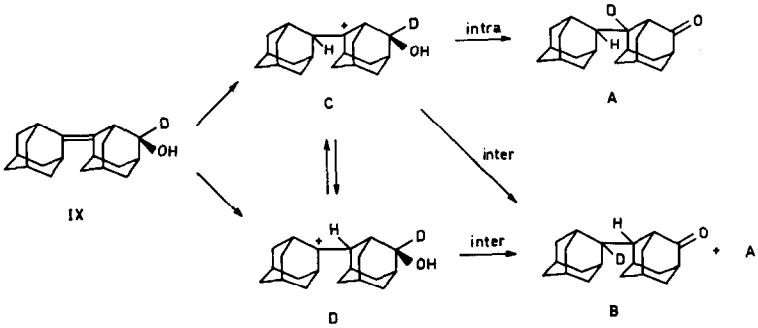


fig.6

An intramolecular process should give only A, while an intermolecular process would be expected give scrambling of deuterium across the central bond because of the fast interconversion of ions

C and D.[9] The product of the rearrangement was examined with CMR and PMR spectroscopy. Comparison of the CMR spectra of the deuterated and undeuterated ketone IV, connected with a calculation of the spectrum with the model compounds 2,2'-biadamantyl and adamantanone, showed that selective deuteration at only one of the two central carbons a and b had occurred (see fig. 1). As mutual assignment between a and b was not possible, $Eu(DPM)_3$ extended PMR spectra of both the deuterated and the undeuterated ketone IV were recorded. From these could be deduced -partly by calculation of the spectrum- that deuteration had occurred carbon b and -by accurate integration- that IV was indeed a single isomer.

All of the three approaches point to an intramolecular 1,3-hydride shift for process 6 (see fig. 2). On this basis it seems reasonable to assume that step 2 is also an intramolecular 1,3-hydride shift.

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