The mechanism for the rearrangement of the adamantyl cation

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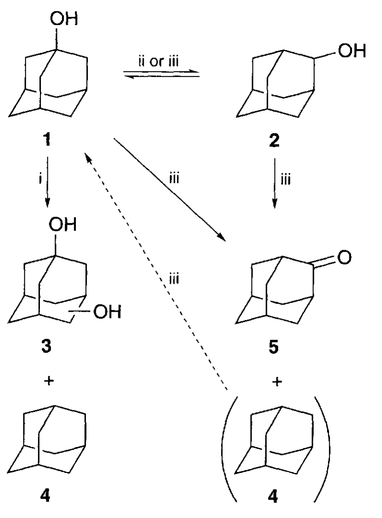
The mechanism for the rapid rearrangement of the adamantyl cation (1-yl → 2-yl, or *vice versa*) in sulfuric acid utilises catalytic adamantane in an intermolecular hydride transfer reaction; a slower rearrangement mechanism involves reversible ring-opening of the adamantyl skeleton, and allows incorporation of high levels of deuterium.

Because of its rigidity and stability, the adamantyl group has been used extensively in many areas of organic chemistry. It now has many applications, including being a key structural unit in polymers, lubricants, pharmaceuticals, and agrochemicals.[1]

Monosubstituted adamantanes are available by free radical substitution of one of the apical hydrogens in adamantane, giving access to 1-substituted derivatives.[2] 2-Substituted adamantanes can be accessed by warming adamantan-1-ol in concentrated sulfuric acid; these conditions establish an equilibrium mixture of 1-ol and 2-ol, from which the 2-ol is removed by oxidation to adamantanone **5** (Scheme 1).[3] The products of this reaction depend critically on the concentration and temperature of the acid (Scheme 1) and, despite the apparent simplicity of the key rearrangement (**1** → **2**), the mechanistic details of this step had not been fully elucidated. It had been inferred that the predominant mechanism for **1** → **2** is not an intramolecular hydride transfer (also disfavoured on grounds of orbital geometry), but is apparently a fast second order reaction (w.r.t. adamantanol, at low concentrations) presumably involving intermolecular hydride transfer.[4] Such a mechanism is consistent with all of the experimental data *except* that disproportionation products would have been expected (*cf.* with dilute sulfuric acid, which generates 1 : 1 ratio of **3** : **4**[5]—see Scheme 1), and this anomaly led us to investigate the rearrangement reaction in more detail. We chose to study the conversion of **2** → **1**, and were able to confirm[6] that the rearrangement follows standard first order kinetics with higher concentrations of **2** ($> 10^{-3}$ mol dm^{-3}), but that the initial rate is apparently dependent on the square of [**2**] at lower concentrations.[†] So what is the mechanism for the rearrangement?

We wondered whether the hydrogens from sulfuric acid might be involved in the mechanism. However, when adamantan-2-ol was dissolved in D_2SO_4, negligible deuterium uptake was observed by the time equilibrium had been reached (*ca.* 2 min). Nevertheless, when the reaction time was extended to several days, multiple deuterium uptake was observed (the major isotopomer possessing 5 deuterium atoms), as indicated by the mass spectrum of the adamantan-1-ol product (Fig. 1). We assume that the mechanism shown in Scheme 2 must be operating; this is further supported by GC–MS results (Fig. 1, inset), showing that a maximum of 12 deuterium atoms were taken up, as would be expected if the diene **8** reformed the adamantyl skeleton **9** *via* 2° → 3° carbocations as shown, leading to deuteriation at the bridging positions (*cf.* deuteriation at the apical positions would have had to proceed *via* 1° → 2° carbocations). Usefully, this procedure offers a simple method of preparing polydeuteriated adamantane derivatives. However, deuterium incorporation was very slow compared with the rate of formation of adamantan-1-ol, indicating that a different, lower energy mechanism for rearrangement was also operating.

We next investigated whether adamantane itself was mediating the rapid rearrangement reaction, as shown in Scheme 3. However, when adamantane was added to the reaction mixture, no increase in the rate of rearrangement was observed. However, careful analysis of the adamantan-2-ol starting material revealed it to be contaminated with a trace (*ca.* 1%) of adamantane. When this was rigorously removed by column



Scheme 1 *Conditions*: i, 70% H_2SO_4 (aq); ii, c. H_2SO_4, room temp.; iii, c. H_2SO_4, heat

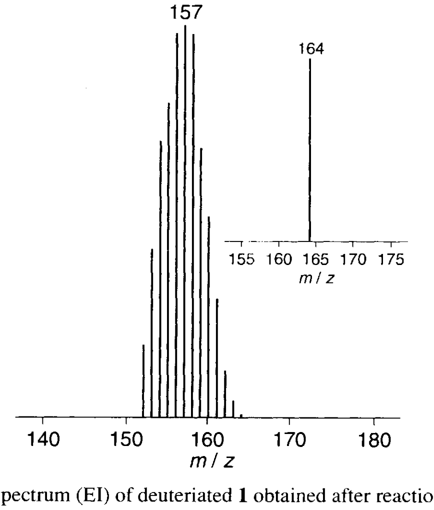
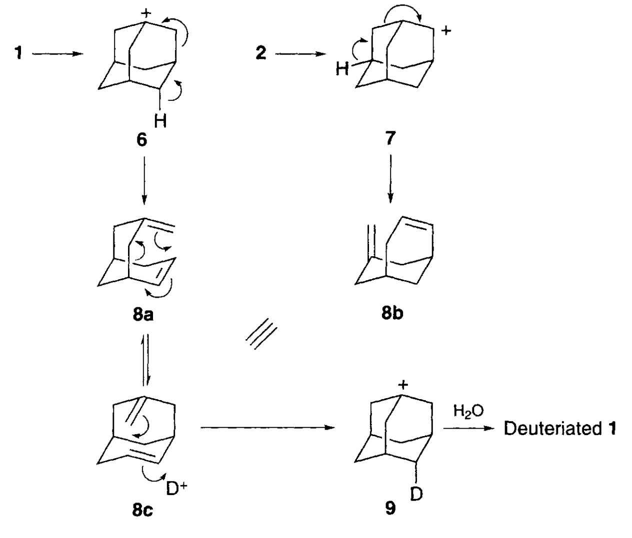


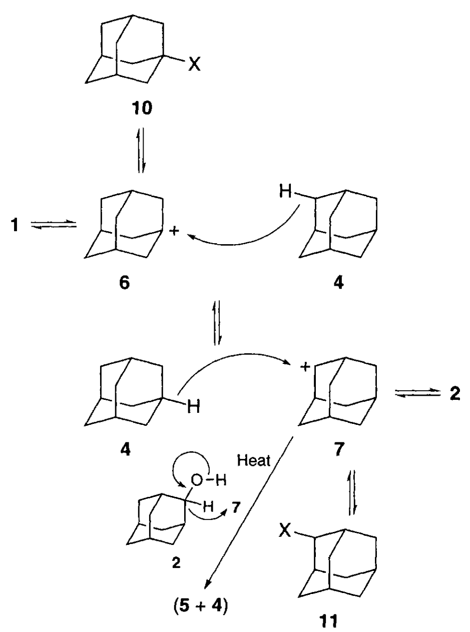
Fig. 1 Mass spectrum (EI) of deuteriated **1** obtained after reaction of **2** with D_2SO_4 over several days; *m/z* for adamantanol = 152. Inset: mass spectrum of the deuteriated **1** that eluted most rapidly by GC–MS. Subsequent fractions had lower deuterium incorporation, with the total ion response corresponding to Fig. 1.

chromatography, the *initial* rate of rearrangement was found to be suppressed substantially, and this initial rate could be restored by the addition of adamantane to the pure adamantan-2-ol. The reaction was not totally quenched, however, because small amounts of adamantane were generated spontaneously in the reaction mixture (seen by GC–MS), presumably *via* reactions shown in Scheme 1.

How do these mechanistic results explain the observed products from the reaction of adamantan-1-ol **1** or 2-ol **2** with sulfuric acid under various conditions? We believe these are neatly summarised in Scheme 3. With concentrated sulfuric acid, almost all of the adamantyl species in solution are cationic {carbocations **6** and **7**, plus protonated hydroxy and sulfate derivatives **10** and **11**, as evidenced by the ^{13}C NMR spectrum [δ_C in H_2SO_4: 255.9, 97.0 (br), 46.5, 43.3, 41.0 (br), 37.4 (br), 34.4, 33.9 (br), 31.4 (br), 28.4(br) and 26.5, with no signals at δ 50–90]}. Hydride abstraction from such cations is presumably slow, and thus catalytic adamantane **4** provides the hydride source. At low concentrations, the contamination of **2** by the catalyst **4** leads to the initial rate being apparently dependent on the square of [**2**]; in fact, $d[\mathbf{1}]/dt = k[\mathbf{2}]$, where k is proportional to the concentration of the catalyst **4**. At about 10^{-5} mol dm^{-3} in adamantane, the solution is saturated with this catalyst, and the reaction then follows standard first order kinetics in **2**; the addition of more adamantane fails to cause any increase in reaction rate, whereas rigorous removal of the adamantane contaminant in **2** leads to a decrease in the initial rate of reaction. With warm concentrated sulfuric acid, the 1-ol/2-ol equilibrium is quickly established, and the slower disproportionation can operate. This generates adamantanone and adamantane; the latter can further catalyse the 1-ol/2-ol rearrangement, but is also susceptible to oxidation to adamantan-1-ol by the sulfuric acid, allowing >50% oxidation of adamantan-1-ol to adamantanone. However, with 70% sulfuric acid, the solubility of adamantane is negligible; under these conditions, any carbocation generated can only abstract hydride from (neutral) adamantanol, thereby generating dihydroxy-adamantane and adamantane (as a precipitate) in a 1 : 1 ratio.



Scheme 2 Mechanism for incorporation of deuterium into adamantanol using D_2SO_4; note that **8b** and **8c** are identical



Scheme 3 Mechanisms for the reactions of adamantanol with sulfuric acid; for **10** and **11**, X = $[OH_2]^+$ or $[OSO_2OH_2]^+$

These mechanisms therefore provide plausible explanations for the various rearrangement reactions involving adamantyl cations, and are consistent with extensive experimental data from ourselves and others (*loc. cit.*).

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Footnote

† Reactions were typically run for 1 min with vigorous shaking, and quenched by the addition of water. The products were analyzed by GC–MS, with the ratio of **2** : **1** being used to determine the extent of the reaction; perfect first order dependence on [**2**] was observed at high concentrations, but as concentrations of **2** were decreased below 10^{-3} mol dm^{-3}, the initial rate decreased more rapidly than expected for a simple first order reaction. Three problems were apparent concerning the quantitative determination of reaction kinetics; the low solubility of the adamantane derivatives (making 'concentrations' uncertain), differences in the precise water content of the concentrated sulfuric acid (98%) and variations in the composition of trace impurities in different batches of **2**. However, repeat runs using specific batches of sulfuric acid and adamantanol under identical reaction conditions (quantities, added water, agitation, duration and temperature) gave highly reproducible results, allowing us to conduct comparative studies with confidence.

References

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