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REVERSIBLE METHIDE SHIFTS IN THE 2-TERT-BUTYL-2-ADAMANTYL CATION

James L. Fry* and James A. Saba

Bowman-Oddy Laboratories, Department of Chemistry

The University of Toledo, Toledo, Ohio 43606

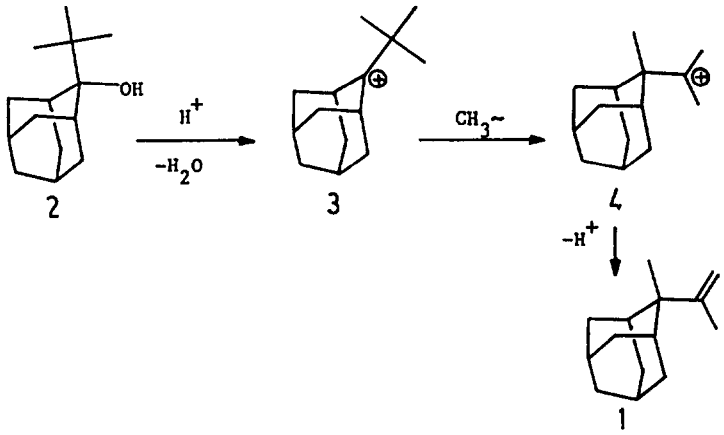
Abstract: Treatment of either 2-tert-butyl-2-adamantanol or 2-isopropenyl-2-methyladamantane with acid in the presence of a reducing agent (hydrogen iodide or tri-n-hexylsilane) yielded 2-tert-butyladamantane as the major or exclusive product. Both precursors gave the 2-tert-butyl-2-adamantyl cation at -78°C in FSO_3H-SbF_5-SO_2ClF.

2-tert-Butyl-2-adamantyl p-nitrobenzoate reacts rapidly in aqueous solvolytic media to give the methyl-shifted alkene 2-isopropenyl-2-methyladamantane, 1, as the major (> 80%) product along with minor amounts of the unrearranged parent alcohol 2-tert-butyl-2-adamantanol, 2.[1,2] Treatment of 2 with traces of acid causes a complete conversion to 1.[1] These results have been understood in terms depicted in Scheme I.

The driving force for the dehydration of 2 as well as the solvolytic behavior of its ester derivative is believed to be the formation of the relatively unstrained cation 3 from sterically strained 2. Since direct loss of a β-proton from ion 3 would result in the formation of an extremely strained bridgehead alkene, a methyl rearrangement to produce ion 4 which can undergo proton loss to yield the observed alkene 1 seems to be a more favorable reaction pathway. That ion 3 is a discrete precursor to the methyl-shifted ion 4 was indicated by the disparity of the deuterium kinetic isotope effects in the overall rate of solvolysis (1.11) versus methyl migration (1.25) during the solvolysis of the p-nitrobenzoate ester which was deuterated at all tert-butyl methyl groups.[2]

We have now discovered that ions 3 and 4 appear to be easily interconverted and that under reducing conditions, product is obtained which is derived primarily or exclusively from ion 3. When a solution of 0.1 g of alcohol 2 in 10 mL of carbon tetrachloride was saturated with hydrogen iodide at room temperature, 2 was immediately converted to alkene 1. However, after one hour, VPC analysis of the dark reaction mixture indicated that only 4% of the originally formed alkene 1 remained, the rest of the reaction mixture consisted of 93% of a major new product and 3% of a minor product.

Scheme I

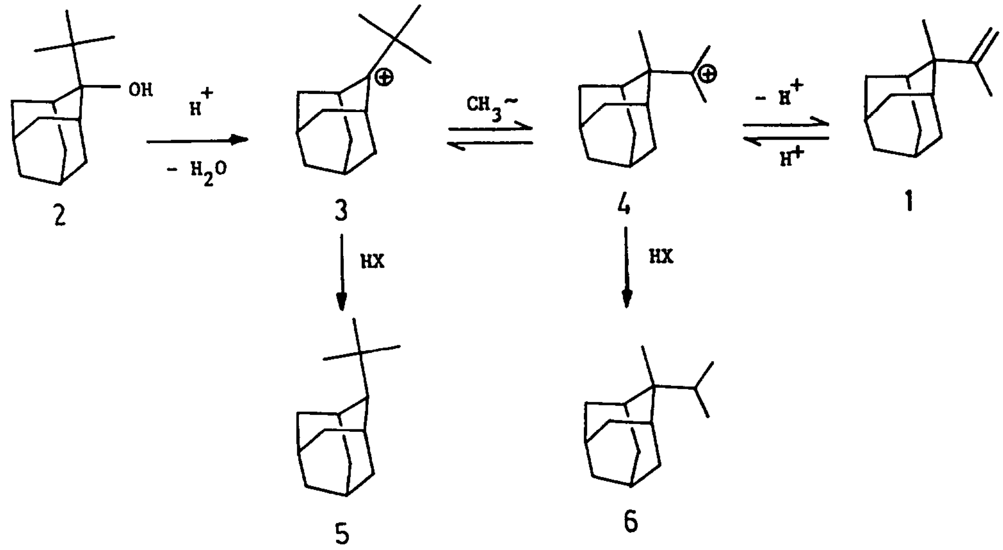


The major product had spectral properties identical with those of previously reported 2-tert-butyladamantane, 5.[3-5] The minor product had spectral properties identical with those of a known sample of 2-isopropyl-2-methyladamantane, 6,[6] which was prepared by hydrogenation of 2-isopropenyl-2-methyladamantane, 1. When alcohol 2 (0.25 g) was treated with 1 eq of tri-n-hexylsilane and trifluoroacetic acid (2.5 mL) in dichloromethane (20 mL),[7] 2-tert-butyladamantane was the only product formed (90%).

The results of these experiments may be understood in terms of the mechanism presented in Scheme II. The postulation of the reversible nature of the methide shift connecting ions 3 and 4 is given credence by a deuterium exchange study. Treatment of a chloroform solution of alkene 1 with DCl for 5 min at 25°C resulted in the recovery of 1 which had incorporated deuterium into it. The ^1H NMR spectrum of this product had diminished height and reduced integration for the signals for the 2-methyl group (δ 1.10), allylic methyl group (δ 1.70), and vinylic hydrogens (δ 4.79, 4.87). The proton-decoupled ^2H NMR spectrum further verified the incorporation of deuterium by showing signals at δ 1.10, 1.70, 4.79, and 4.89. The proton-decoupled ^{13}C NMR spectrum showed the loss of three signals (δ 109.7, 26.0, and 19.0) which were replaced by small diffuse humps. The fact that deuterium was found on the 2-methyl group of 1 indicates that 3 and 4 are interconvertible.

Stable carbocation solutions were prepared from compounds 1 and 2 in FSO_3H-SbF_5-SO_2ClF and were examined by ^1H and ^{13}C NMR spectroscopy. Both of the solutions produced the same

Scheme II



spectra, were stable for at least 24 hr at -78°C, and did not undergo any appreciable spectral changes in the temperature range of -78 to -20°C Both the ^1H and ^{13}C NMR spectra obtained[8,9] were very similar to those reported for the 2-methyl-2-adamantyl and 2-ethyl-2-adamantyl cations[10] and were quite consistent with the structure of a stable 2-tert-butyl-2-adamantyl cation (**3**) There was no evidence of any appreciable amount of ion **4** in these solutions

These results are in accord with molecular mechanics calculations performed by Schleyer and Chang which indicate that ion **4** has 6.7 kcal mol^{-1} more strain energy than does ion **3** and hydrocarbon **6** has 3.3 kcal mol^{-1} more strain energy than does even the relatively strained compound **5**.[11,12]

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References and Notes

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5 ^{13}C NMR ($CDCl_3$) δ 54 6, 42 2, 39 0, 34.1, 33 4, 30 7, 29.9, 29 2, and 28 1, mass spectrum m/e 135 (base), 192 (M^+)

6. ^{1}H NMR ($CDCl_3$) δ 0 75 (6 H, d, J = 6 8 Hz), 0 82 (3 H, s), 1 3 - 2 2 (14 H, br m), 2 4 (1 H, sept , J = 6 8 Hz); ^{13}C NMR δ 15 78, 15 81, 27 91, 28 18, 29.28, 32 56, 33 98, 34.05, 39.25, 40.11.

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8 ^{1}H NMR δ 2.04 (9 H, s), 2 57 (4 H, s), 3.10 (8 H, ABq), 4 60 (2 H, s), ^{13}C NMR δ 26 2 (q), 28 3 (d), 35 5 (t), 50.4 (t), 57.5 (d), 59 4 (s), 317.8 (s)

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