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EXCEPTIONALLY HIGH BARRIERS TO 1,2-HYDRIDE SHIFTS IN THE 1-ADAMANTYL CATION

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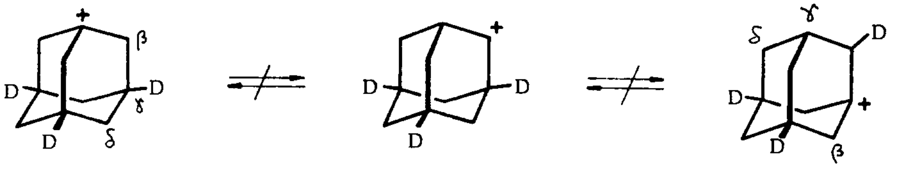
Intramolecular 1,2-shifts are strongly inhibited on the adamantane nucleus.[1,2] The "vacant" carbonium ion orbitals of both the 1- and the 2-adamantyl cations are rigidly held in conformations unfavorable for such migrations.[1,2] Hydride shifts occur intermolecularly, if at all,[1a] and apparent 1,2-alkyl migrations involve instead more complex skeletal isomerization processes.[1b,c] We have now attempted in a new way to determine the barrier height of such adamantyl 1,2-shifts. At 130°C a lower limit of 10 sec^{-1} for the rate of proton interchange in 1-adamantyl cation[3] is established by NMR line shape analysis[2,4]; consequently: Ea >20 or 22 kcal/mol (with log A = 12 or 13) is set for an eventual proton-mixing process.



I II III

We wished to see whether hydrogen scrambling could be observed in the 1-adamantyl cation on the chemical time scale. Accordingly the 3,5,7-d_3-1-adamantyl cation (I) was prepared by adding at -100°C in vacuo a solution of the corresponding chloride in SO_2ClF (prepared[5] from 3,5,7-d_3-1-adamantyl bromide[6]) to a solution of SbF_5 in SO_2ClF. As the pmr spectrum of I lacked the downfield peak (ca. δ = 5.5ppm) characteristic of the γ(bridgehead) protons[3], proton scrambling by inter- or intramolecular routes had not occurred during cation generation[6].

No γ-proton signal due, e.g., due to the possible equilibria $I \rightleftharpoons II \rightleftharpoons III$ was observed after heating I at 105°C for 90 minutes. If a pmr detection limit of 5% is accepted, less than 10% of scrambling must have occurred; thus a lower limit for the scrambling rate constant is

2×10^{-5} sec^{-1} leading to the minimum activation barrier estimates: Ea >29 or 30.5 kcal/mol (with log A = 12 or 13). These limits should be contrasted with the moderate barriers (Ea = 15 kcal/mol) typically encountered for 1,2-hydride shifts in analogous acyclic ions.[2,7]

Based on heat formation[8], solvolytic rate data and conformational analysis calculations[9], the bridgehead 1-adamantyl cation (e.g. I and III) is expected to be somewhat less stable than the t-butyl cation, and the 2-adamantyl (e.g. II) cation more stable than the isopropyl cation.[10] Thus, the energy difference between I (or III) and II should be less than the typical 15 kcal/mol secondary-tertiary energy difference.[2,5,7,8,10] This means that the barrier to rearrangement II→I or III should be appreciably greater than 15 kcal/mol, i.e., it should be possible to observe the 2-adamantyl cation directly. Thus far, we have failed in all attempts to do so, perhaps because of local heating effects or a rapid intermolecular chain process producing isomerization during cation formation. From a variety of potential 2-adamantyl cation precursors, only the 1-adamantyl cation was observed.

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