Mechanism of Acid Catalysed Opening of the Cyclopropane Ring in the Thujols

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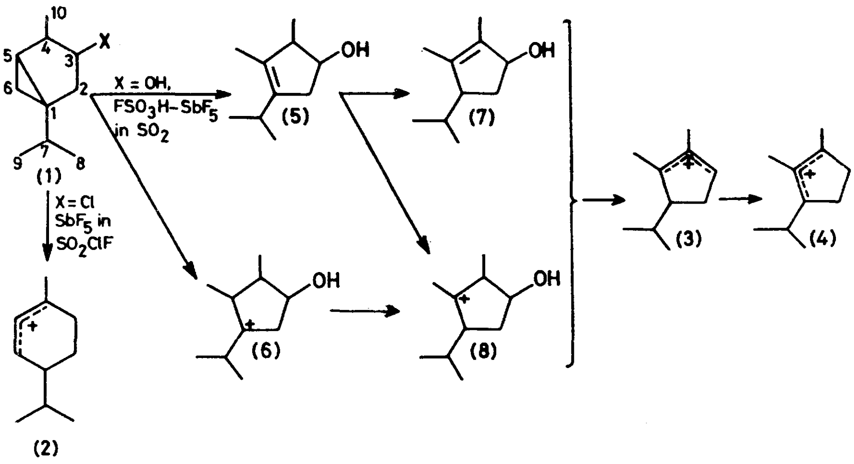
Summary Formation of a cyclopentenium ion from the thujols with super acid has been shown by deuterium labelling studies to involve at least two routes.

Reaction of all the isomeric thujols (**1**, X = OH) with FSO_3H–SO_2 at −80 °C has been shown to give the cyclopentenium ion (**3**), which subsequently rearranges to (**4**). This reaction has been postulated to proceed *via* acid catalysed opening of the cyclopropane ring to form the olefin (**5**), followed by double bond shift and ionisation.[1]

Evidence that reaction is not initiated at the alcohol group on C-3 has been obtained by comparing the reaction of the alcohol (**1**, X = OH) with FSO_3H–SbF_5–SO_2 at −80 °C with the reaction of the chloride (**1**, X = Cl) with SbF_5 in SO_2ClF at −80 °C. The latter reaction proceeds *via* generation of a carbocation at C-3, and follows a completely different pathway from reaction of the alcohol with acid, yielding the cyclohexenium ion (**2**). However, opening of the cyclopropane ring of the alcohol with deuteriated acid should yield a deuteriated product; Olah[2] working on the parent system, treated bicyclo[3.1.0]-hexan-3-ol with DF–SbF_5 and was unable to detect any deuterium incorporation. On treating (**1**, X = OH) with FSO_3D–SbF_5–SO_2 at −80 °C, we were unable to detect any deuterium incorporation into the ion (**3**), though partial incorporation or extensive scrambling would render it undetectable by either the ^{13}C or the ^1H magnetic resonance spectroscopy techniques used.

To check for scrambling, we labelled, successively, positions 2, 3 and 4 in (**1**, X = OH). On treatment with FSO_3H–SbF_5–SO_2 at −80 °C, the labels in positions 2 and 3 remained intact in the substituted cyclopentenium ion (**3**), but that on position 4 was lost. Reaction of (**1**, X = OH) in which the three hydrogen atoms on carbon atoms 2 and 4 were replaced by deuterium with FSO_3D–SbF_5–SO_2 at −80 °C gave (**3**) in which C-7 was deuteriated, and the hydrogen on C-1 was largely (*ca.* 80%) replaced by deuterium.

Failure to incorporate deuterium specifically on C-6 when (**1**, X = OH) is treated with FSO_3D–SbF_5 rules out protonation on C-6 followed by breaking of the C-1 to C-6 bond as the only mechanism of ring opening. The most probable main mechanism is opening of a face or edge protonated species, accompanied by an internal shift of hydrogen to form an olefin directly. Formation of the olefin (**5**) is consistent with incorporation of deuterium onto C-7 by exchange with deuteriated solvent, and reaction *via* olefin shift to (**7**) or protonation to (**8**) would lead to the observed ion (**3**). However, the first process would transfer a label from C-4 to C-1 specifically and the second would completely label C-1 in a deuteriated acid; since neither reaction of (**1**) deuteriated on C-4 with FSO_3H nor reaction of unlabelled (**1**) with FSO_3D gives (**3**) with detectable deuterium labelling on C-1, then both processes must in fact proceed simultaneously. Even so, reaction of (**1**, X = OH) deuteriated at C-4 with FSO_3D does not completely label C-1, so that some species other than the olefin (**5**) must be involved in the process. This species must also be able to exchange the hydrogen on C-7 with deuteriated solvent, which makes the ion (**6**), formed by protonation of C-6 and ring opening, the probable intermediate in this minor pathway.



Scheme

To investigate further this mechanism, we treated the chloride (**1**, X = Cl) with FSO_3H–SbF_5–SO_2 and obtained the ion (**3**). We then carried out the reaction at −90 °C, and looked for the chloro-carbocation corresponding to (**8**). It was not observed; only (**3**) could be seen. However, for the parent chloride, *cis*-bicyclo[3.1.0]hexan-3-yl chloride, reaction with FSO_3H–SbF_5–SO_2 at −70 °C gave the methyl cyclopentenium ion, but reaction at −90 °C gave this ion together with the 3-chloro(methyl)cyclopentenium ion.[3] On warming the solution to −50 °C, the chloro-carbocation decomposed to yield only the methyl-cyclopentenium ion.

Reaction of (**1**), X = H) with FSO_3H was found to follow a different pathway from ring opening of the thujols, and gave the ion (**4**) directly.

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