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FLUOROSULFURIC ACID INDUCED CYCLISATION OF A METHALLYL CARBINOL INVOLVING AN APPARENT OXYGEN MIGRATION

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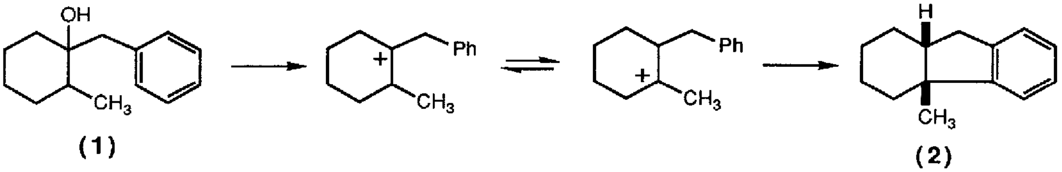
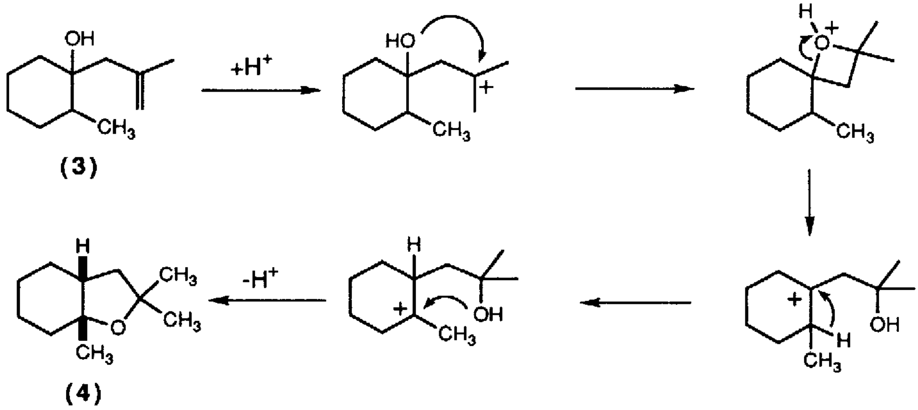
Summary: The methallyl carbinol **3** reacts with HSO_3F to give the cyclic ether **4**, via the intermediacy of a protonated oxetane.

As part of an continuing study[1-4] of the use of superacids in organic synthesis we recently described[3] the reactions of a series of benzyl carbinols with fluorosulfuric acid at -78°C. A variety of different reaction modes were found to occur, depending on the specific substrate. For example the 2-methylcyclohexanol **1** underwent rearrangement and cyclisation to give the hexahydrofluorene **2** in >85% yield. We have since[4] extended this study by replacing the benzyl group with 2-phenylethyl and 3-phenylpropyl substituents and now report a further extension in the form of the methallyl carbinol **3**.



Reaction of **3** with HSO_3F at -78°C, quenching and product isolation gave 2,2,7a-trimethyl-*cis*-octahydrobenzofuran **(4)**,[5] as the only monomeric product.[6] The formation of cyclic ethers in HSO_3F has been the subject of considerable recent attention.[7-10] In the present case the



product ether cannot be formed by a direct cyclisation reaction since the oxygen has undergone an apparent migration. The mechanism shown accounts for this by cyclisation of the initially formed cation to produce a protonated oxetane which is unstable under the reaction conditions[11] and which undergoes ring opening to a new hydroxy cation which, after a hydride shift, recyclises[12] to the observed product.

This represents the first example of cyclic ether formation in HSO_3F in which the oxygen atom undergoes migration during the course of reaction. The reaction is also novel in that it is the first case of cyclisation in HSO_3F to produce an oxetane (albeit as an intermediate) and the first example of a tertiary hydroxyl group cyclising to an ether in HSO_3F.[13]

References and Notes

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(5) ^1H NMR ($CDCl_3$, 300MHz) : 2.19 (m, H3a), 2.00 (t, J = 12.5 Hz, H3-ax), 1.68 (m, H3-eq), 1.65-1.36 (H4-H7), 1.34 and 1.20 (2 x s, C2-CH_3's), 1.27 (s, C7a-CH_3). ^{13}C NMR ($CDCl_3$) 20.9 (C5), 24.1 (C4), 25.3 (C6), 26.4 (C7a-CH_3), 30.8 and 31.2 (C2-CH_3 's), 36.4 (C7), 42.5 (C3), 43.6 (C3a), 78.6 (C2), 81.2 (C7a).

(6) In addition considerable polymerisation occurs; the ether **4** was obtained in ca 40% yield.

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(11) Previous attempts[9] to generate oxetanes in HSO_3F from diols or allylic alcohols gave only polymeric products. Indeed we obtained only polymeric products from 1-methallylcyclohexanol (i.e. the corresponding substrate lacking the 2-methyl substituent).

(12) This ring opening/ring closure has a precedent in the recently reported[8] ring contraction of 1,8-cineole to 1,4-cineole in HSO_3F.

(13) It has previously been concluded[8] that cyclic ether formation can occur in HSO_3F by intramolecular interaction of a carbocation with a primary or secondary hydroxyl group but that tertiary hydroxyls lead to allyl cations.

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