Rearrangements of 2,3-Epoxy-Cis-Pinane in Acid Media

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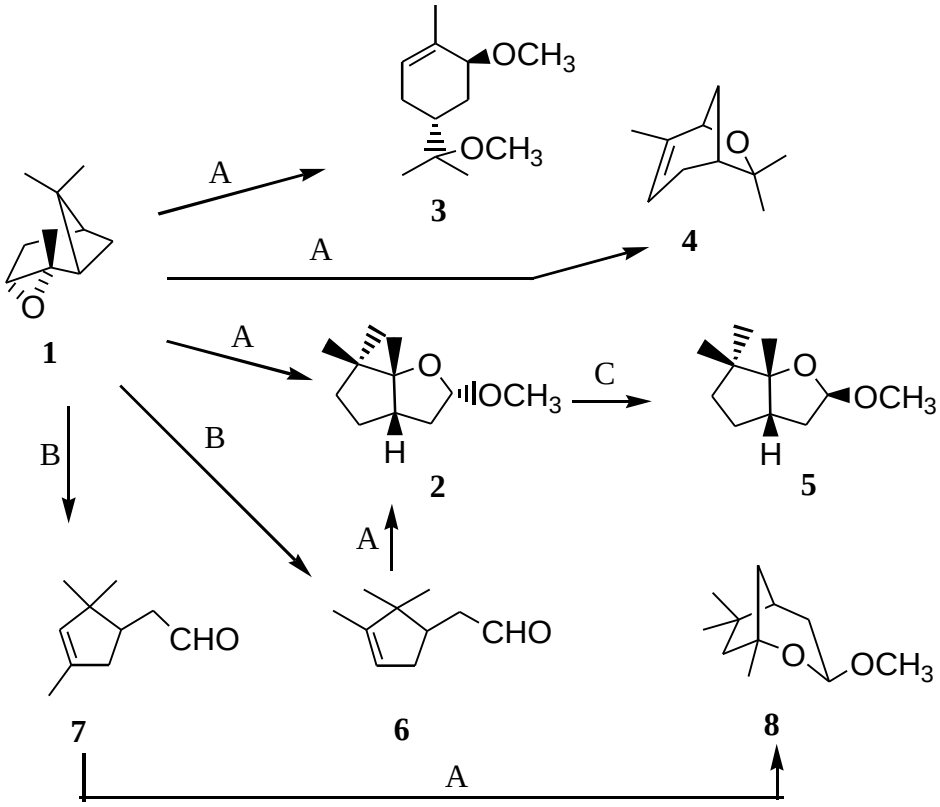
When «quenched» by a CH_3OH-$(C_2H_5)_2O$ mixture in an HSO_3F-SO_2FCl mixture (-110 °C), 2,3-epoxy-cis-pinane 1 is transformed into a mixture of compounds 2, 3, 4. Previously, compounds 3 and 4 were not isolated in decomposition reactions of epoxide 1 in acid media; according to our data, compound 2 was not reported in the literature. A mechanism of this reaction is proposed using molecular mechanics and quantum chemical calculations.



A - HSO_3F-SO_2FCl; B -zeolite-β; C - SiO_2

In the presence of beta-type zeolite (20 °C), epoxide 1 isomerizes into a mixture of aldehydes 6 and 7 (in a ~5:1 ratio (GLC), respectively). Transformations of aldehydes 6 and 7 in the HSO_3F-SO_2 system (-110 °C) have been studied. In these conditions, the aldehydes are transformed into bicyclic acetals 2 and 8, respectively; this agrees with the mechanism which we suggested for the rearrangement of epoxide 1 in superacids.

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