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

Marina P. Polovinka, Dina V. Korchagina, Yurii V. Gatilov, Oleg G. Vyglazov, and Vladimir A. Barkhash

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences., 9 Lavrentiev ave., 630090 Novosibirsk 90; polovina@nioch.nsc.ru

When «quenched» by a CH₃OH-(C₂H₅)₂O mixture in an HSO₃F-SO₂FCl 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.

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 HSO₃F-SO₂ 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.