Reactions of Cis- and Trans-Epoxides (+)-3-Carene and Limonene with Aldehydes on Askanite-Bentonite Clay

Konstantin P. Volcho, Lyudmila E. Tatarova, Dina V. Korchagina, Nariman F. Salakhutdinov, and Vladimir A. Barkhash

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

As is known, treatment of 3-carene and limonene epoxides with mineral acids gives diols, which are solely the products of trans-diaxial cleavage of the epoxide ring (no cis-diols were observed).

Here it is shown that the reactions of cis- and trans-epoxides of (+)-3-carene (scheme 1), limonene (scheme 2), and dipentene with aldehydes in the presence of askanite-bentonite clay at 0°C lead not only to isomerization products but also to acetals whose hydrolysis selectively affords the corresponding cis-diols.

In these transformations, steric factors determine the ratio between the intra- and intermolecular processes and hence the set of reaction products. Using a clay - aldehyde system, we managed to selectively obtain the products of cis-cleavage of the epoxide ring in mild conditions with yields of up to 70%. This reaction may be of practical interest in cases where it is desirable to selectively obtain cis-diols, leaving other functional groups intact and avoiding formation of skeletal rearrangement products.