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

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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.