SYNTHESIS AND REACTIONS OF OPTICALLY ACTIVE 6,8-DIOXABICYCLO[3.2.1]-OCTANES DIRECTED TOWARD THE SYNTHESIS OF PYRANOID NATURAL PRODUCTS

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Optically active pyranoids from the tetrahydro-derivatives to δ-lactones have been used as the versatile synthetic intermediates for a variety of optically active compounds and appear as the important functional group in many biologically active compounds. Recently we have developed a new method for the short-step synthesis of optically active 6,8-dioxabicyclo[3.2.1]octanes (A) from dialkyl tartrate by utilizing the inherent C_2 symmetry of tartrate. Here we report several aspects in the approach to the functionalized pyranoids (B) from A.

The bicyclic compounds (A) with 7-exo-substituents were easily prepared from tartrate and 3-arylsulfonyl acetals by way of four- or five-steps sequence of reactions. The behaviors of A against the conditions of 1) acetolysis (Ac_2O/BF_3-Et_2O/CH_2Cl_2/0 °C); 2) alcoholysis ($PhCH_2OH/BF_3$-Et_2O/CH_2Cl_2/r.t); 3) reduction with $LiAlH_4$-$AlCl_3$ (Et_2O/reflux); 4) acetal cleavage with mercaptanes (RSH) and Lewis acid (BF_3-Et_2O) (CH_2Cl_2/0 °C, or $ClCH_2CH_2Cl$/70 °C); and 5) the organo-aluminium reagent (Et_2AlSPh/toluene/-40∼-20 °C) were investigated. Under these conditions the 3-sulfonyl and 5-alkyl substituents proved to play crucial roles on the reactions of the bicyclic system (A) as illustrated below. The several pyranoids obtained were utilized for synthesis of biologically active natural products.