

Abstract

A series of five aziridine derivatives of 1,6-anhydrohexoses having *D-manno*, *D-allo*, *D-galacto* and *D-talo* configurations has been prepared via the following synthetic reactions. From 1,6:2,3- and 1,6:3,4-dianhydro- β -D-hexopyranoses, vicinal azido tosylates have been prepared by azidolysis and subsequent tosylation. The aziridine ring was built up by reduction of azido tosylates by NaBH_4 or LiAlH_4 and *N*-substituted derivatives were also prepared. By this sequence the aziridine derivatives have been prepared in 61-67 % yields.

The fluorination by DAST consisted of the reaction of *N*-benzylated epimines having free OH-group in the vicinity of the aziridine ring with diethyl amino sulphur trifluoride (DAST) in dichloromethane. Vicinal fluoro aziridines thus obtained have arisen via direct displacement of DAST-activated hydroxyl group by fluoride. In no case the aziridine ring was affected by DAST. From nine different starting sugar epimines, only two derivatives afforded the desired products with the yields around 45 %.

For fluorination by KHF_2 , activating nosyl group had to be introduced on nitrogen atom of the aziridine ring. The *N*-substitution by 2-nitrobenzenesulfonyl group was done by sulfonylation using 2-nitrobenzenesulfonyl chloride in a triethylamine-tetrahydrofuran mixture at -30 to -40 °C. Yields of the target nosylepimines were in the range 37–93 %.

Aziridine ring-opening reactions of *N*-nosylepimines with potassium hydrogendifluoride under various reaction conditions have been performed to introduce fluoride atom onto sugar skeleton. As predicted by the Fürst-Plattner rule, *trans*-diaxial isomers of the vicinal amino fluoro derivatives of 1,6-anhydro- β -D-hexopyranoses were preferentially formed in 31-90 % yields. For some epimines, diequatorial isomers have been detected in the reaction mixtures.

2-Nitrobenzenesulfonyl group has been removed from products of the cleavage by reaction with benzenethiol and potassium carbonate in an acetone-water mixture. The deprotection has been demonstrated on one fluoro derivative only.

The structure of fluoro derivatives was determined by NMR spectroscopy.