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Stereoselective Synthesis of Dioxabicycles from 1-C-allyl-2-O-benzyl-glycosides — An Intramolecular Cyclization between 2-O-benzyl Oxygen and the Allyl Double Bond

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Abstract

Addition of a proton to the double bond of 1-C-allyl-O-benzylglycosides gave a 2′-carbonium ion, which in turn reacted intramolecularly, in a regio- and diastereo-selective manner, with the nucleophilic oxygen of the 2-O-benzyl group to form an oxonium intermediate. Subsequent cleavage of the benzyl C–O bond led to dioxabicycles in moderate yields. Surprisingly, opposite diastereoselectivities were observed from 1-C-allylglycofuranosides and 1-C-allylglycopyranosides, which produced 2,2′-trans- and 2,2′-cis-dioxabicycles, respectively.Key words: C-glycoside, olefin, cyclization, oxocarbonium, dioxabicycles.