

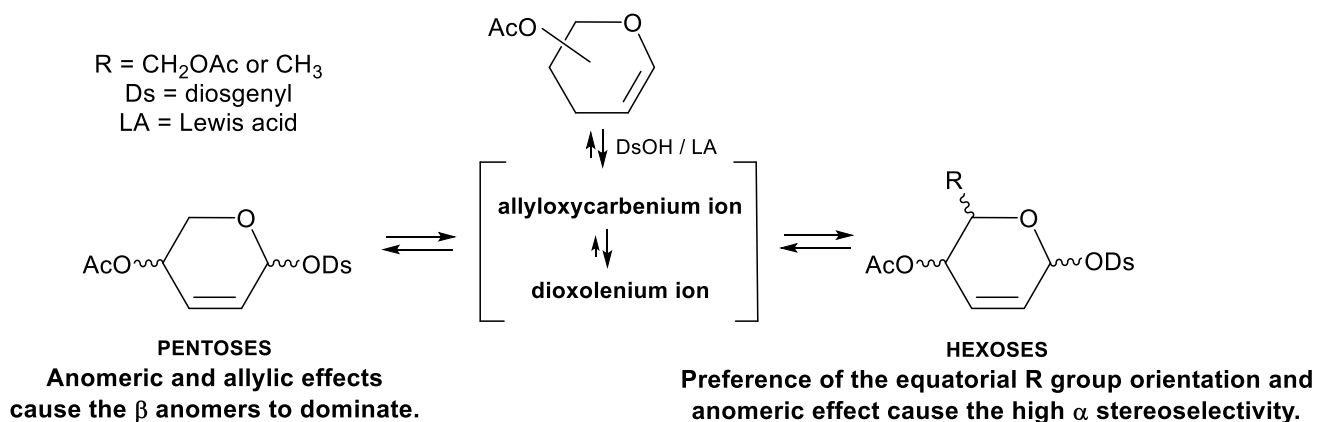
INSIGHT INTO THE COURSE OF THE FERRIER REARRANGEMENT

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The Ferrier rearrangement is a widely explored reaction in which 2,3-unsaturated glycosides are obtained from per-*O*-acetylglycals (Figure) [1-4]. It is known for its efficiency and high α stereoselectivity characteristic of hexoses.

We applied the Ferrier rearrangement to get 2,3-unsaturated diosgenyl glycosides [5]. The diversity of the glycals used in these syntheses allowed us to discuss thoroughly the Ferrier rearrangement mechanism and its stereoselectivity. The DFT calculations were performed to compare stability of the dioxolenium and allyloxycarbenium ions, considered intermediates of the reaction. Presented results indicate that the thermodynamic equilibrium between them is shifted toward the former ion. However, it is the allyloxycarbenium ion which determines the reaction regioselectivity. In turn, stereoselectivity of the Ferrier rearrangement is closely related to the stability of the formed 2,3-unsaturated glycosides associated with the adopted conformation. Factors influencing this stability in the case of hexoses are ranked as the equatorial orientation of the terminal R group > anomeric effect > allylic effect. In the case of pentoses only the last two factors influence the stability of the Ferrier rearrangement products. This causes 2,3-unsaturated hexopyranosides and 2,3-unsaturated pentopyranosides to have different preferences for the anomeric configuration. Presented findings may contribute to the rational design of glycosylation strategies for bioactive glycosides.



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