

Thesis title: Acid-Catalyzed Rearrangement of Vinyl Ethers and Ketene Acetals

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Summary of the doctoral thesis

The [1,3] rearrangement reaction of vinyl ethers (O→C rearrangement), represent powerful method of construction of a new carbon-carbon bond by the breaking carbon-oxygen one. This transformation involves the rearrangement of molecules bearing latent electrophilic and nucleophilic moieties, the in situ molecular fragmentation of which results in the concomitant formation of a stabilized positive charged species and an activated nucleophile. These species re-combine to generate the product by formation of a new carbon-carbon bond. The most prevalent oxygen-to-carbon rearrangements are those whereby the stabilization of positive charge is mediated by an oxygen atom.

I have demonstrated that substituted vinyl acetals and unsymmetrical ketene acetals undergo smooth TMSOTf-catalyzed rearrangement to afford chain-extended ketones or esters. The O→C rearrangement reactions proceed in the presence of very small amounts of an acidic catalyst (1 mol%), for a wide range of substrates which are easily accessible.

In the next step a range of structurally diverse *C*-glycosides has been synthesized, starting from simple and readily accessible anomeric vinyl ethers and ketene acetals precursors, using a [1,3] rearrangement reaction initiated by the Lewis acid. A key observation from these syntheses, was the stereoelectronic interactions made on the success of the rearrangement. Significantly, the rearrangement showed also good levels of diastereoselectivity in the synthesis of *C*-disaccharides.

The optimised methodology was applied towards the diastereoselective synthesis of β -aminoketones and β -amino acids which can be readily transformed into bicyclic β -lactams. Finally, it was found that the vinylogous variant of the title rearrangement is particularly useful for the preparation of cyclohexenes.