

Mukherjee, A.; Jayaraman, N., 2012, "2,3-Unsaturated enoses. A Pummerer rearrangement route to sugar vinyl sulfides and synthesis of 3-deoxy-3-alkyl / arylsulfinyl pyranosides", *Tetrahedron*, 68, 8746 – 8752.

This manuscript deals with a synthetic methodology development to functionalize C-2 and C-3 carbons of pyranosides. The development pertains to the implementation of Pummerer rearrangement on appropriately positioned sugar sulfoxide at C-3 of a monosaccharide. Logical development presented in the manuscript was prompted by an ability to synthesize sugar sulfoxide at C-3. Implementation of a Pummerer rearrangement on sugar sulfoxides, appear to be un-known so far, afforded endocyclic sugar vinyl sulfides that are reactive intermediates for further synthetic manipulations. The potential of sugar vinyl sulfides was demonstrated through conversion to sugar vinyl sulfoxides, followed by undertaking conjugate addition reactions on vinyl sulfoxides, using alkoxides. Conjugate additions across the vinyl sulfoxide functionality were found to be diastereoselective, to afford product with manno-configuration exclusively. Protecting groups on the pyranoside were found to affect the conjugate addition, thus, whereas the reaction was facile with pyranosides having either ester protecting groups or no protecting group, none of the conjugate addition was found to occur with sugar vinyl sulfoxide having ether protecting groups. Further, substituents on the sulfoxide moiety were found to influence the reaction yields, with an aryl substituent providing better yields of the conjugate addition than with an alkyl substituent. Employing such versatile Pummerer rearrangement - conjugate addition reactions in order to achieve monosaccharide modifications opens-up even greater synthetic manipulations of sugars.