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Diastereodivergence in the acyloxyallylation of protected and unprotected aldoses

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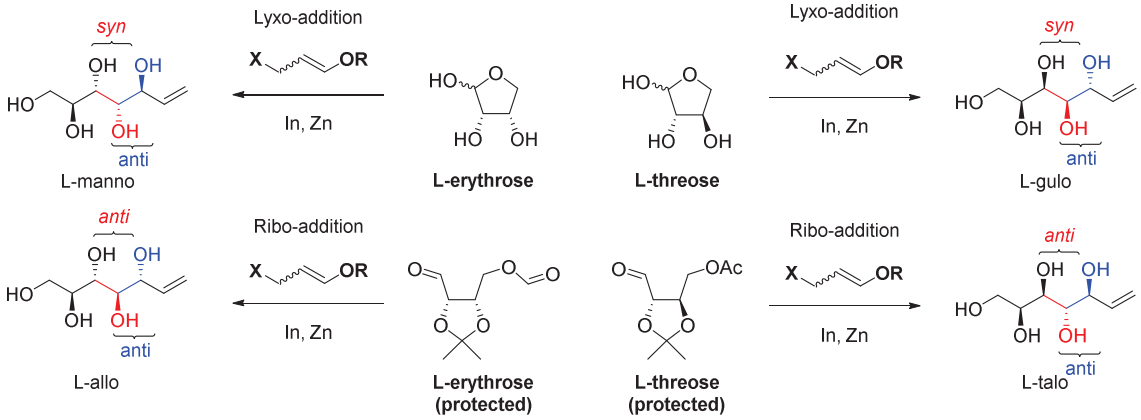
The indium mediated acyloxyallylation of aldoses, introduced by the Madsen group a decade ago is an elegant way for the two-carbon elongation of reducing sugars (upon ozonolysis).[1] In this prove-of-concept study, the standard D-pentoses and D-hexoses were used as starting materials, giving rise to heptoses and octoses, respectively. Isolation of the main isomer showed that out of the four possible diastereomers, the product with lyxo-configuration (*syn*, *anti* - addition) is dominant in all cases investigated.

Recently, we have developed this methodology into the first short synthesis of L-glycero-D-manno heptose at scale starting from L-lyxose. Within this study we also elucidated the two other diastereomers formed, thus identifying the type of selectivity observed when applied to reducing sugars.[2]

To expand on this, we set out to engage in an in-depth methodological investigation. We chose the L-tetroses as starting materials in order to obtain L-hexoses as products, for which authentic samples are available, allowing unambiguous identification.



We found a comparable selectivity with L-erythrose and L-threose. Furthermore, a pronounced diasterodivergenz was found whether or not 2O,3O-protection was in place in the starting material. We evaluated the effect of steric bulk in the reagent on the diastereoselectivity in a systematic manner and could even achieve transformation with cheap zinc instead of indium. However, a complete loss of selectivity was observed, rendering this otherwise attractive modification useless.

As a synthetically valuable side-line, we could establish a short scalable protocol towards L-allose, representing a second example of an exotic sugar made more readily available *via* acyloxyallylation.

1) Palmelund, A.; Madsen, R., *J. Org. Chem.* **2005**, *70*, 8248-8251

2) Stanetty, C.; Baxendale, I. R., *Eur. J. Org. Chem.* **2015**, *2015*, 2718-2726

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