

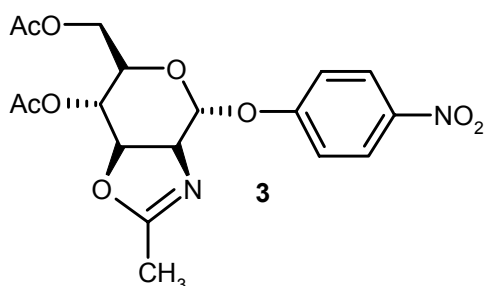
## SYNTHESIS OF 4-NITROPHENYL 2-AZIDO-2-DEOXY- AND 2-ACETAMIDO-2-DEOXY-D-MANNOPYRANOSIDES AND MECHANISM OF STAUDINGER REDUCTION

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Generally, a variety of 4-nitrophenyl D-hexopyranosides has been exploited as efficient chromogenic glycosyl donors for chemoenzymic synthesis of oligosaccharides. A combination of nucleophilic substitution and glycosylation represents an easy synthetic route to 4-nitrophenyl 2-azido-2-deoxy-D-mannopyranosides in a gram scale and high overall yield. Subsequent reduction with hydrogen sulfide readily provides respective 4-nitrophenyl 2-acetamido-4,6-di-O-acetyl-D-mannopyranosides (**1** and **2**).[1] These selectively protected compounds could be useful tool for *N*-acetyl mannosamine-containing oligosaccharides synthesis.

During the course of our study we found that reaction of both 4-nitrophenyl 3,4,6-tri-O-acetyl-2-azido-2-deoxy-D-mannopyranosides with Ph<sub>3</sub>P followed by hydrolysis gave surprisingly mannopyranosides **1** and **2** as well. Although the Staudinger reduction of acetylated azido sugars seems to be a routine strategy, no deeper mechanistic study was carried out. Consequently, the course of the reaction was checked by <sup>31</sup>P, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and by MS measurement and results were confronted with preparative experiments. Approximate kinetics for the successive stages of reaction and identification of the intermediates are discussed.



We found that the Staudinger reaction was followed by aza-Wittig reaction providing oxazoline **3**.

### Acknowledgement

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[1] Popelova, A.; Kefurt, K.; Hlavackova, M.; Moravcova, J. *Carbohydr. Res.* **2005**, *340*, 161-166.