

Selective mono-O-alkylation (protection) of carbohydrates catalyzed by stannylene acetals

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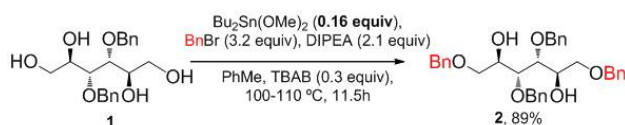
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INTRODUCTION

Carbohydrates and their derivatives play important roles in nature.¹ The use of such natural materials in the synthesis of complex oligomers,² analogues, or chiral building blocks (in total synthesis) depends on efficient methodologies for selective protection.³

Previously, we had demonstrated that selective O-alkylation of polyols may be catalyzed by stannylenes. Thus, di-O-benzylation of D-mannitol derivative **1** was carried out efficiently with low load of the tin reagent (only ~15 mol% of depolymerized Bu₂SnO was used) (Scheme 1).⁴

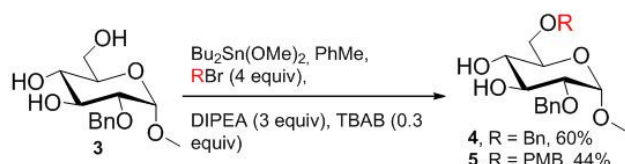


Scheme 1. Seminal result of catalysis by stannylenes.⁴

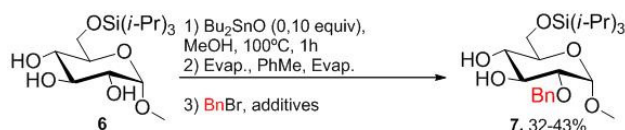
Thus, this study aims at the selective mono-protection (O-alkylations) of carbohydrates using stannylene acetals as catalysts.⁴

RESULTS AND DISCUSSION

Initial experiments employing even lesser amounts of the tin reagent (10 mol%), for the most part, indicated the need of optimization of our original protocol (Schemes 2, 3).

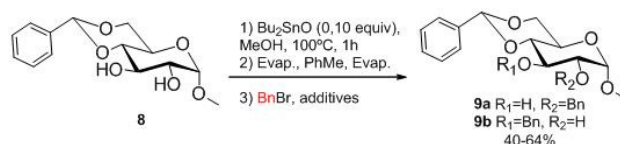


Scheme 2. Selective protection of O-methyl D-glucoside **3** catalyzed by stannylenes.



Scheme 3. Selective protection of O-methyl D-glucoside **6** catalyzed by stannylenes.

Thus, notwithstanding the expected formation of regioisomers, we used resisting substrate **8** as model for the protocol optimization (Scheme 4). With this work, we managed to attain good yields of **9**. The results and the investigation strategy will be discussed.



Scheme 4. Model reaction for the optimization of the catalytic reaction.

CONCLUSION

The feasibility of selective monoprotection (via O-alkylation) of carbohydrates catalyzed by stannylenes was established.

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