

Synthesis of *O*-Glycosides Dimers Catalysed by Tellurium (IV) Tetrachloride

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Keywords: *O*-glycosidation, *O*-glycoside dimers, tellurium tetrachloride

INTRODUCTION

The α -2,3-Unsaturated-*O*-Glycopyranosides are important building blocks in the synthesis of several natural products, glycopeptides, carbohydrate derivatives, oligosaccharides, and nucleosides.¹

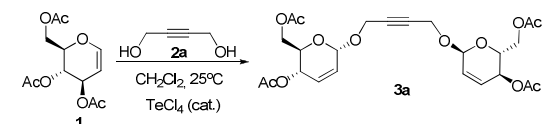
The synthesis of this class of compounds is generally based on the glycosidation reaction, which involves a nucleophilic substitution reaction combined with an allylic shift in a glucal. A number of Lewis acids and oxidizing agents can promote the reaction. These methods, however, present some drawbacks such as low yields and lack of selectivity.

The ongoing interest in constructing libraries of highly glycosylated compounds that can mimic specific oligosaccharide-protein interactions prompted us to further search for efficient routes based on the use of tellurium tetrahalides toward glycosylated building blocks.²

RESULTS AND DISCUSSION

For preliminary optimization of the reaction conditions, glucal **1** and diol **2a** in dichloromethane were treated at room temperature with different amounts of tellurium catalyst and the progress of the reaction was monitored by TLC. The results are depicted in Table 1.

Table 1. Influence of the amount of tellurium catalyst in the synthesis of 2,3-unsaturated *O*-glycoside, **3a**^a

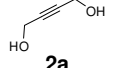
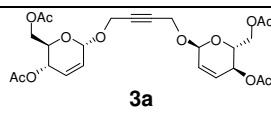
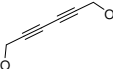
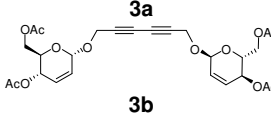
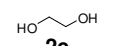
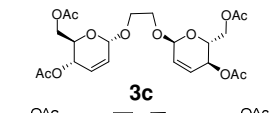
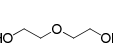
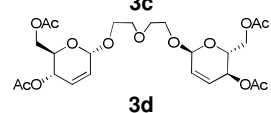
			
	catalyst(mol%)	Time (h)	Yield(%) ^a
1	-	12	-
2	TeBr ₄ (10)	0.25	81
3	TeBr ₄ (5)	0.25	76
4	TeCl ₄ (5)	0.10	88
5	TeCl ₄ (2)	0.10	89

^a isolated yield

When tellurium tetrahalides were used, the reaction proceeded smoothly leading to the complete conversion of **1** into the desired product with almost exclusive α -anomeric selectivity. Better yields were observed when TeCl₄ was used as catalyst.

In order to demonstrate the efficiency of this reaction, we explored the generality of our method extending the conditions to other diols and the results are summarized in Table 2.

Table 2. TeCl₄ promoted synthesis of 2,3-unsaturated *O*-glycosides **3a-d**

	HO-R-OH	Product	Yield (%) ^a
1			89
2			76
3			70
4			67

^a isolated yield

The reaction gave the desired products in good yields and with α -anomeric selectivity in all cases, being the stereochemistry of the products confirmed by the NOe experiment.

CONCLUSION

In summary, we have demonstrated the use of a catalytic amount of TeCl₄ as the Lewis acid choice to promote the *O*-glycosylation of glucals. The glycosides were synthesized under mild conditions, excellent yields and good α -anomeric selectivity.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge CNPq, CAPES, FACEPE and INCT-INAMI for the financial support.

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