



SYNTHESIS OF 2,3-UNSATURATED O-GLYCOSIDES MEDIATED BY ULTRASOUND IRRADIATION

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Keywords: O-glycosides, Ferrier reaction, Ultrasound

INTRODUCTION

Lewis acid-catalyzed allylic rearrangement of glycals in the presence of alcohol is well known as the Ferrier reaction¹ and widely employed to obtain the 2,3-unsaturated glycosides. 2,3-Unsaturated-O-glycosides are also important building blocks in the synthesis of some antibiotics.² The Ferrier rearrangement involves the intermediacy of an allylic oxycarbenium ion to which the nucleophile adds preferentially in a quasi-axial orientation. The Lewis acid catalysts used for this rearrangement include BF₃·OEt₂, SnCl₄, FeCl₃, DDQ, NIS, I₂, acidic Montmorillonite K-10, BiCl₃, InCl₃, Sc(OTf)₃ and Yb(OTf)₃, Sc(OTf)₃ and Yb(OTf)₃ and [Bi(OTf)₃]. In recent years have also been employed for the Ferrier rearrangement the tellurium (IV) tetrachloride.³ In the paper, we set out to explore the potential of *p*-tolyl sulfonic acid for the preparation of 2,3-unsaturated O-glycosides through Ferrier rearrangement of 3,4,6-tri-O-acetylglucal, mediated by ultrasound irradiation.

RESULTS AND DISCUSSION

The reaction of alcohols **2a-h** with 3,4,6-tri-O-acetylglucal **1**, carried out in presence of catalytic amount of *p*-tolyl sulfonic acid mediated by ultrasound irradiation, afforded the corresponding 2,3-unsaturated glucopyranosides **3a-h** (table 1). In all cases the compounds were obtained as a mixture of α - and β -anomers. The selectivity α/β was small influenced by the catalyst used and was in favor of α -anomers. the ratio of α/β anomers is shown in Table 1. To explain the major formation of α -anomers, Shostakovskii et al.⁴ suggested that the reaction should be proceeded by a mechanism involving the anchimeric assistance of the acetate group at C-6 on the anomeric center. This assistance involved an allylic rearrangement reaction and departure of acetoxy group at C-3, followed by the nucleophilic attack at C-1 by the lower face to give 2,3-unsaturated glycosides. The α/β anomers selectivity was also enhanced with the length of carbon chain.¹ H and ¹³CNMR spectra of all

the compounds were in conformity with those reported values.³

Table 1- Reactions of 3,4,6-tri-O-acetyl-D-glucal with various alcohols using *p*-tolyl sulfonic acid as catalyst.

Entry	Products (3a-h)	Time (min)	Rate (α/β)	Yield(%)
1		5	88:12	82
2		5	88:12	98
3		5	89:11	93
4		5	98:2	50
5		5	86:14	85
6		5	86:14	60
7		5	98:2	73
8		10	91:9,1:9	74

CONCLUSION

In summary, we have developed a highly stereoselective, *p*-tolyl sulfonic acid catalyzed Ferrier glycosylation to produce 2,3-unsaturated glycosides. Compared to other methods, our method appears to have advantages such as good yields, high anomeric selectivity, shorter reaction times, mild reaction conditions and low catalyst loadings.

ACKNOWLEDGEMENTS

The authors are grateful to the CNPq, FACEPE and CAPES for financial support.

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