

## STEREOSPECIFIC SYNTHESIS OF GLYCOSYL CHLORIDE USING A COMBINATION OF BISMUTH NITRATE AND BISMUTH CHLORIDE

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**Abstract:** Stereoselective synthesis of glycosyl chloride has been achieved using a combination of bismuth nitrate and bismuth chloride.

**Keywords:** Glucose Peracetate, Catalysis, Stereochemistry

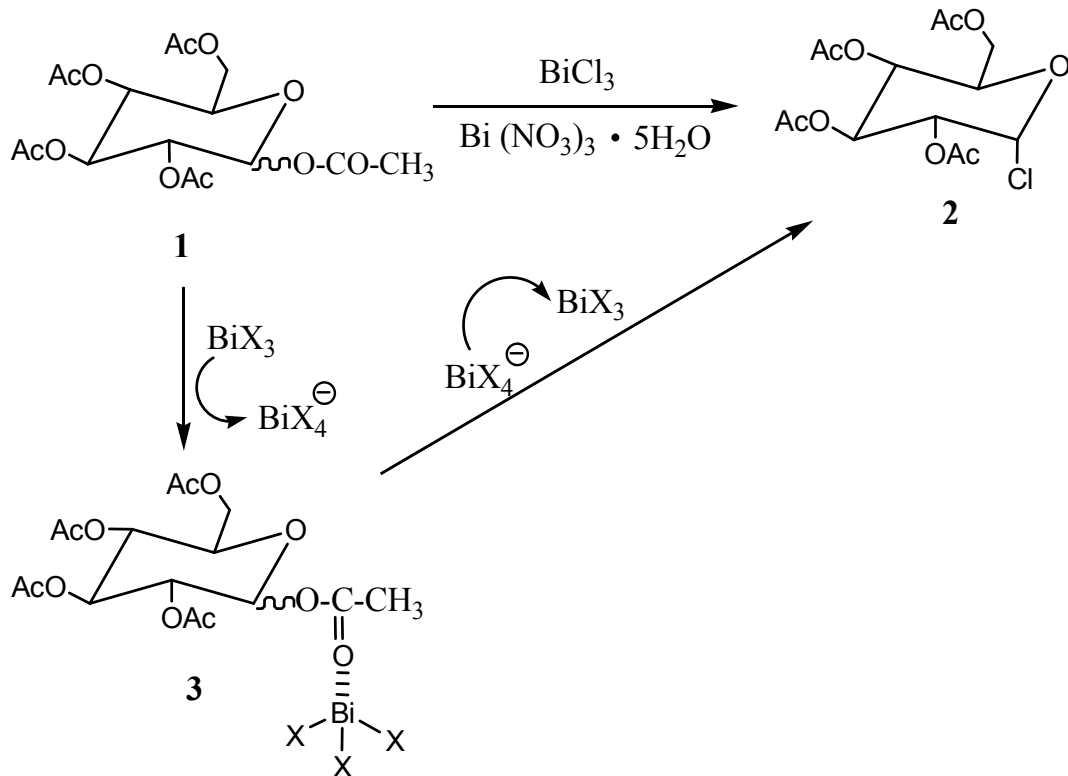
**Introduction:** Glycosyl chloride is of interest for the preparation of diverse glycosides. The carbon-halogen bonds can be converted to cationic, anionic and radical intermediates.<sup>1, 2, 3</sup> A number of reports are known for the preparation of glycosyl chlorides. These include methods using reagents, such as hydrogen chloride, acetyl chloride, aluminum chloride, zinc chloride, titanium tetrachloride, phosphorous pentachloride and thionyl chloride. We report here a new method for the preparation of glycosyl chloride by reacting peracetylated glucose and galactose using a combination of bismuth nitrate pentahydrate-bismuth chloride.

**Results and Discussions:** Peracetylated glucose (**1**) and peracetylated galactose (**2**) on reaction with bismuth chloride in the presence of catalytic amounts of bismuth nitrate pentahydrate (10 mol%) in dry dichloromethane produced the chloride derivatives **2** and **5** in 80% yields at room temperature (**Scheme 1** and **Scheme 2**). We believe bismuth nitrate forms a coordinate bond with the oxygen of the acetate group present in the anomeric center as shown in **3**. A nucleophilic attack can then be possible and this acetate group can then be removed by attack of the anion of bismuth trichloride. In principle, the formation of the product should be possible in the absence of bismuth nitrate since bismuth chloride, itself, can also coordinate with the oxygen of the anomeric acetate group. However, the yields of the chloride **2** and **5** were not satisfactory when bismuth chloride was used alone (**Scheme 1**). This suggests that the coordinating power of bismuth nitrate is much superior to bismuth chloride.

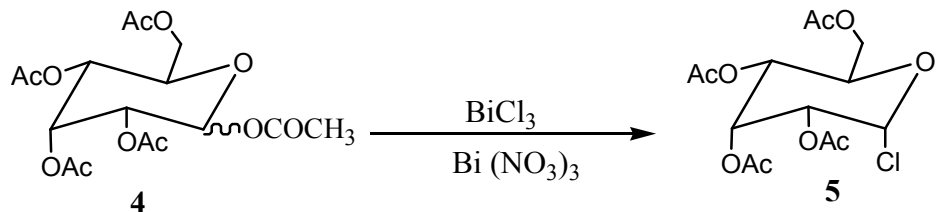
Interestingly, the reaction is highly stereospecific and produces only one anomeric product. The formation of the beta-isomer is not observed.

Bismuth salts are not toxic, highly economical and stable in air. The work-up procedure of this reaction is easy and the products are pure enough to use for further reactions. An extension of this method for the preparation of other glycosyl halide (bromide and iodide) will be undertaken in the future. Despite much success of bismuth salts-catalyzed reactions, their used synergistic effects have not been investigated.<sup>4</sup>

### Scheme 1



### Scheme 2



**Conclusion:** A simple and rapid stereospecific synthesis of glycosyl chloride using catalytic amounts of bismuth nitrate and bismuth chloride has been accomplished in good yields.

**Acknowledgements:** We gratefully acknowledge the financial support for this research project from National Institutes of Health-SCORE (2SO6GM008038-37) and (NCIP20CA138022).

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