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SYTHESIS OF GLUCOSE PERACETATE VIA BISMUTH NITRATE-INDUCED REACTION

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Abstract: Simple synthesis peracetylated glucose has been achieved starting from glucose and acetic anhydride in the absence of solvent via bismuth nitrate-catalyzed reaction. This method does not need large excess of acetic anhydride.

Keywords: Glucose Peracetate, Catalysis, Stereochemistry

Introduction: Per-O-acetylated pyranose sugars are very valuable building blocks for the synthesis of natural products, glucoconjugates and oligosaccharides.¹ Structural elucidation of natural and synthetic products is often facilitated by transformation of their per-O-acetates. Peracetylation of sugars require acid or base as reagents/catalysts and an excess of acetic anhydride in the presence of large amounts of solvents.² In continuation of our research on bismuth nitrate-catalyzed reactions, we report here a facile synthesis of glucose peracetate starting from beta-glucose and glucose (stereochemistry is not defined) at the anomeric position.³

Results and Discussion: Bismuth nitrate pentahydrate has been used for peracetylation reaction due to its unique properties of being readily affordable, commercially available, ecologically friendly and low toxicity. Reaction of β-δ-glucose (1) was performed with 5.5 equivalents of acetic anhydride in the presence of 10 mol% bismuth nitrate pentahydrate in solventless conditions. The reaction mixture was heated to 60° C for 2h. In another experiment, the reaction mixture was kept at room temperature for 48h. An identical procedure was followed with glucose (3) in which stereochemistry of anomeric carbon is not defined. It is interesting to note the formation of β-isomer (2) from the first reaction. However, the reaction produced a mixture of isomers (2) and (4) in equal proportion in 80% yield when 3 was the substrate (**Scheme 1**).

We hypothesize that the peracetylation of sugar can proceed due to a coordination of bismuth nitrate with acetic anhydride and thereby it serves as a promoter. Due to lanthanide contraction bismuth salts exhibit Lewis acidity. The glucose peracetates 2 and 4 are important starting compounds for the glycosylation of oxygen, nitrogen and carbon-containing compounds. In this reaction, slight excess of acetic anhydride has been used. Most conventional methods use large excess of acetic anhydride as a regent in the presence of a solvent while also using other

acid/base catalysts in larger quantities. Notably, our procedure was conducted in the absence of any solvent and proved to be effective. In contrast to conventional Lewis acids, bismuth nitrate is economical, non-toxic, stable and commercially available. On the basis of these advantages, our method will find application in synthetic and carbohydrate chemistry. The stereochemistry of 2 and 4 can be easily deduced from their NMR data.

Scheme 1

OH OH OH
$$OHOO$$
 $OHOO$ $OHOOO$ $OHOO$ $OHOO$

Conclusion: We have demonstrated that bismuth nitrate can be used for the peracetylation of glucose under environmentally benign conditions.

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