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NOVEL MECHANISM OF INDIUM METAL-INDUCED GLYCOSYLATION WITH β-LACTAMS

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Abstract:
This perspective describes indium metal-induced glycosylation of bromosugar with 3-hydroxy beta lactam alcohol. The unique mechanism of this reaction is also advanced.

Introduction:
Indium-induced reactions have become very fascinating. We have described numerous indium-assisted reactions for the past many years. A successful stereospecific glycosylation of bromosugar with 3-hydroxy β-lactam has been performed. The mechanism of this reaction is discussed.

Results and Discussions:
We have been actively engaged in the chemistry of indium and β-lactams [1, 2]. An indium-induced stereospecific preparation of oxygen glycosides was conducted with diverse alcohols and bromosugar. It was also used to thioglycosylate bromoglucose stereosepecifically [3]. Indium-mediated reaction of 3-hydroxy β-lactams with bromoglucose gave two diastereomers of β-O-glycosides [4]. Most of the other glycosylations produced α-isomers. Therefore, this observation is interesting. An explanation is required for this type of observation. Indium-assisted reaction of β-lactam alcohol and bromo sugar followed a unique mechanism.

The indium-induced glycosylation can follow two mechanisms: nucleophilic unimolecular and nucleophilic bimolecular. Nucleophilic unimolecular pathway can generate a carbocation at the anomeric carbon through the departure of the bromine. The carbocation can then react with the hydroxyl nucleophile from the top and bottom side of the sugar. These attacks obviously should produce two isomers in different proportions depending upon the stability of the intermediates. On the other hand, the alcohol nucleophile can attack the α-bromosugar from the top phase and this can generate product with a β-confuguration. It seems that the attack from the top-phase is feasible under the conditions of this reaction. This suggests that bromine of the bromosugar is

not able to form a complex with indium metal because such a complex would not be ideal for a nucleophilic attack to the anomeric carbon because this carbon will be partially negative in charge, if it happens. Instead, it looks like a simultaneous departure and bimolecular substitution nucleophilic attack by the alcohol from the opposite side of the bromine is a favorable path in this reaction.

The stereochemical study of glycosylation is also investigated by other reagents and catalysts [5]. Some of the products have considerable anticancer activities [6].

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