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2-Amino Sugar Synthesis via Rhodium-Complexed Nitrenes

The main objective of our research is to study nitrogen atom transfer, synthesizing biologically active 2-amino sugar derivatives through amidoglycosylation reactions. Such syntheses are valuable because 2-amino sugars exist as components of oligosaccharides in biological systems. The amidoglycosylation strategy involves the formation of rhodium-stabilized nitrene intermediates from glycal 3-carbamates. These intermediates insert into the carbon-carbon double bond of the glycal. The reaction is completed when the glycosyl acceptor alcohol stereoselectively attacks the anomeric carbon to produce the 1,2-trans addition product (Scheme 1). To produce the 1,2-trans product (**2**) selectively from starting galactal 3-carbamate (**1**), the alcohol attacks from the bottom face of a glycosyl aziridine intermediate. Under these amidoglycosylation conditions, a significant amount of byproduct **3** formed via C3–H oxidation. The anomeric stereocontrol and chemoselectivity in the amidoglycosylation reactions is partially a function of the 4O and 6O protecting groups. With acetyl protecting groups as in **1**, a 1:1 mixture of amidoglycosylation product **2** to byproduct **3** formed. The 1,2-trans amidoglycosylation product **2** and byproduct **3** were identified using NMR analysis and mass spectrometry. Varying the protecting groups as well as the catalyst led to changes in chemoselectivity of the amidoglycosylation reaction.

SCHEME 1