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Novel Glycosylation of Aromatic Amines Through 1, 2-Anhydrosugars

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Abstract

A new and novel bismuth nitrate and indium bromide-catalyzed glycosylation of aromatic amines with glycal epoxides is described in moderate yield. Despite the poor nucleophilicity of the aromatic amines, the success of this reaction is noteworthy.

Keywords: Glycosylation; Amine; Epoxide; Catalyst

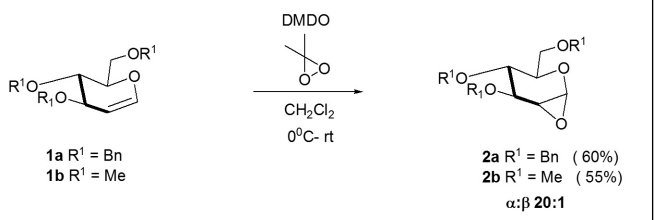
Introduction

Acid-catalyzed glycosylation of alcohols and thiols is an attractive field of research. The nucleophilicity of alcohols and thiols is high enough to react with an anomeric center of a sugar system that has an alkene, hydroxy or halogen group [1-12]. It is necessary to activate the reactants by acidic catalysts. However, glycosylation of aromatic amines with the above mentioned sugar derivatives are extremely difficult. Aromatic amines are much less nucleophilic compared to alcohols and thiols. In this communication, a simple bismuth nitrate and indium bromide-catalyzed reactions of 1,2-anhydrosugars and diverse aromatic amines is described [13-39]. The success, although not excellent, deserve special attention as synthesis of these types of molecules is not known. Moreover, the method for aromatic glycosylation is not investigated.

Results and Discussion

Glycosylation of β-lactam alcohols and other alcohols were studied by our group [1-12]. This was performed with iodine-catalyzed and indium metal-catalyzed reactions of alcohols and glycal or bromo sugar derivatives. The success of this reaction was excellent. In parallel studies, bismuth nitrate and indium bromide were also investigated as catalysts for the glycosylation reaction of aromatic amines. Aromatic primary amines are widely distributed in nature. Perhaps, aromatic primary amines are the most widely studied functional groups in chemistry. However, carbohydrates bound to aromatic amine through its anomeric center and the nitrogen of the amine is difficult to obtain. To overcome the shortcomings, the reaction of aromatic amines with sugar epoxide was chosen.

At the beginning of this approach protected sugar epoxide 2 was prepared from glycal 1 by DMDO-catalyzed oxidation reaction (Scheme 1). The epoxide 2 on reaction with different aromatic primary amines in the presence of bismuth nitrate and indium bromide afforded the sugar-linked NH-aryl systems 3 (α-isomer) and 4 (β-isomer) in moderate yield. The ratios of the β-isomers were much higher than the ratios of the α-isomers irrespective of the nature of the solvents and catalysts used in these reactions (Scheme 2 and Table 1). In general, it was found that glycal epoxide was consumed within 2-6 h.



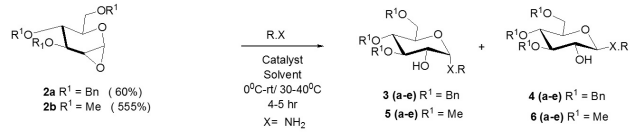
Scheme 1: DMDO mediated oxidation of Glycals. Synthesis of 1,2-Anhydrosugar (Glycal epoxide).

Entry	Epoxide	Catalyst	Solvent(s)	Amine(x) (x=N)	Yield (%) isolated	Ratio (a:b) 3 and 4	Time (hrs)
1	1a R^1=Bn	$Bi(NO_3)_3.5H_2O$	THF	Aniline	30	3a+4a(1:9)	4
				p-Anisidine	60	3b+4b(1:9)	3
				p-Toludine	55	3c+4c(1:9)	3
				9-AP	35	3d+4d(2:8)	5
				6-AC	30	3e+4e(3:7)	6

	1a R^1=Bn	$InBr_3$	CH_2Cl_2	Aniline	60	3a+4a(1:9)	3
				p-Anisidine	70	3a+4a(1:9)	2
				p-Toludine	65	3a+4a(1:9)	2
				9-AP	45	3a+4a(2:8)	4
				6-AC	40	3a+4a(3:7)	5
2	1b R^1=Me	$Bi(NO_3)_3.5H_2O$	THF	Aniline	45	5a+6a(1:9)	3
				p-Anisidine	65	5b+6b(1:9)	2
				p-Toludine	50	5c+6c(1:9)	2
				9-AP	40	5d+6d(2:8)	4
				6-AC	30	5e+6e(3:7)	5
	1b R^1=Me	$InBr_3$	CH_2Cl_2	Aniline	50	5a+6a(1:9)	3
				p-Anisidine	60	5b+6b(1:9)	2
				p-Toludine	55	5c+6c(1:9)	2
				9-AP	35	5d+6d(2:8)	4
				6-AC	50	5e+6e(3:7)	5

Table 1: Reaction condition and products ratios of the nucleophilic ring opening of glucal epoxide. 9-AP (9-Aminophenantherene); 6-AC (6-Aminochrysene).

The reaction proceeded with monocyclic to tetracyclic primary aromatic amines. Polyaromatic compounds, like 9-aminophenanthrene and 6-aminochrysene are extremely weak nucleophiles and sterically hindered. It was very interesting to note that these polyaromatic primary amines reacted with sugar epoxide in the presence of bismuth nitrate and indium bromide. To our knowledge carbohydrates directly linked to the amino group of aromatic compounds is not known. In our earlier studies, polyaromatic amino compounds were used as anticancer agents [40-43]. However, structurally the compound described herein is totally different than our previous compounds.



Scheme 2: Stereo selective ring opening of glucal epoxide with N nucleophile. A facile high stereo selective synthesis of N glycoside.

The formation of β-isomer is explained by the nucleophilic attack of the aromatic amino group from the opposite face of the sugar epoxide. This type of attack is favored because of the steric hindrance imposed by the aromatic ring. Since cleavage of an epoxide ring is possible from both sides of this functional group, formation of minor amounts of α-isomer is also observed.

Conclusion

A method of aromatic amino glycosylation reaction with sugar epoxide in the presence of bismuth nitrate and indium bromide is achieved in moderate yield. This reaction is totally unknown and therefore, there is an enormous possibility to study this reaction. For example, identification of other catalysts, temperature, protective group in sugars and alteration of the nucleophilicity of the aromatic amines can be undertaken. Nevertheless, the present study opens up a new method for the preparation of several unknown molecules. On the basis of the biological activities of related molecules, we expect to publish the full paper in this field in the future.

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