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INDIUM-INDUCED HIGHLY STEREOSELECTIVE THIOGLYCOSYLATION OF PERACETYLATED BROMOGLUCOSE

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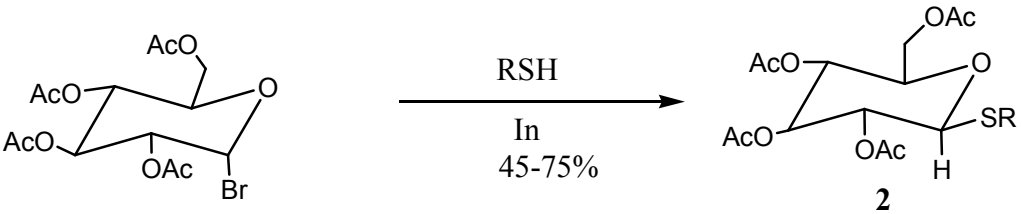
Abstract: A highly stereoselective synthesis of thioglycoside has been accomplished starting from bromo peracetylated glucose and thiol in the presence of indium.

Keywords: Indium, Bromo Peracetylated Glucose, Stereoselective

Introduction: Glycosylation is an attractive area of research because of the complexity of the precudure.[1] Therefore, an effective methodsof glycosylation development is necessary.[2] The glycosyl fluoride[3a] and thioglycoside[1] method and Ferrier rearrangement[3b] are the recognized processes for this purpose. Several Lewis acids[4] and acidic support[5] have been used succesfully. Nonstereoselectivty of the reaction is a major concern to chemists. Attempts have been made to improve the stereoselectivity of these processes.[6,7] Our exploration in this field resulted in a convenient method of stereoselective synthesis of β-thioglycosides via reaction of thiols with β-D-bromoglucose derivatives mediated by indium metal.[8]

Results and Discussion: Some of these methods for thioglycosylation have proved to be effective; however, they still have limitations including, lengthy synthesis of the donor or the acceptor, the use of toxic activators and unstable activating agents. Therefore, development of easily accessible, non-toxic, environmentally friendly activators is highly desirable. In this paper, we report a stereoselective synthesis of β-D-glycoside with indium metal. Organometallics, such as zinc, samarium diiodide, and titanium reagents, produced the glycals when treated with β-D-bromoglucoses.

Scheme -1

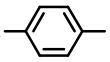


1 **2**

a : R = CH_3CH_2-

b: R = $CH_3CH_2CH_2$-

c: R = 

d: R= H_3C 

Reaction of thiophenol and methylthiol with 2,3,4,5,6-penta-*O*-acetyl-α-D-glucopyranosyl acetate (**1**) in the presence of bismuth nitrate using tetrahydrofuran (THF) as the solvent produced glycosides **2** in 80% yield (**Scheme 1**). The anomeric stereochemistry was determined to be β from the coupling constant of the anomeric hydrogen (7.5-10.0 Hz).

Conclusion: Indium-mediated glycosylation has produced highly stereoselective thioglycoside with aliphatic and aromatic thiols and acetobromoglucose.

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References:

1. K. Toshima and K. Tatsuta. *Chem. Rev*. **93**, 1503 (1993)
2. R. R. Schmidt. *Agnew Chem*. **98**, 213 (1986)
3. K. Toshima. *Carbohydr. Res*. **327**, 15 (2000)
4. P. Bhate, D. Horton and W. Priebe. *Carbohydr. Res*. **144**, 331, (1985)
5. K. Toshima, T. Ishizuka, G. Matsuo and M. Nakata. *Synlett.* **306** (1995)
6. For some recent examples of α-anomer, see: (a) M. Bols. *J. Chem. Soc*., *Chem Commun*. 913 (1992). (b) B. K. Banik, M. S. Manhas and A. K. Bose, *J. Org. Chem*. **59**, 4714 (1994). (c) B. K. Banik, M. S. Manhas and A. K. Bose. *Tetrahedron Lett*. **38**, 5077 (1997). (d) B. K. Banik, O. Zegrocka, M. S. Manhas, A. K. Bose. *Heterocycles*. **46**, 173 (1997)
7. For some recent examples towards β-anomer, see: (a) W. Roush and C. E. Bennett, *J. Am. Chem. Soc*. **121**, 3541 (1999). (b) B. Yu and Z. Yang. *Tetrahedron Lett.* **41**, 2961 (2000)
8. For some indium induced reactions, see: (a) B. K. Banik, M. Suhendra, I. Banik and F. F. Becker. *Synth. Commun*. **30**, 3745 (2000). (b) B. K. Banik, S. Samajdar, I. Banik, O. Zegrocka and F. F.Becker. *Heteroycles*. **55**, 227 (2001). (c) B. K. Banik, I. Banik, L. Hackfield and F. F. Becker. *Hetereocycles*. **56**, 467 (2001)