Chinese Chemical Letters Vol. 14, No. 3, pp 233 – 234, 2003
http://www.imm.ac.cn/journal/ccl.html

A Facile Approach to Regioselective 1-*O*-Deacylation of Peracylated Glycopyranoses

Jia Qiang DONG, Shu Jia ZHANG, Yan Guang WANG*

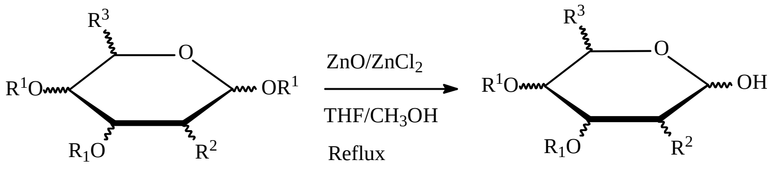
Department of Chemistry, Zhejiang University, Hangzhou 310027

Abstract: The regioselective 1-*O*-deacylation of peracylated glycopyranoses **1a-d** with zinc chloride and zinc oxide in THF/MeOH gave the corresponding tetra-*O*-acylglycopyranoses **2a-d** in good yields.

Keywords: 1-Hydroxy sugars, oligosaccaride, zinc chloride.

Suitably 1-hydroxy sugars are important materials and valuable building blocks for the preparation of various glycosyl donors in the synthesis of oligosaccharides and glycoconjugates[1-3]. The hydrolysis of acylglycosyl halides was a classical method for preparation of 1-OH peracylated glycopyranoses[4]. This method involves a two-step reaction sequence in which in the first step, D-glycopyranose pentaacetates are converted to unstable glycosyl halides, and in the second step, the halides are hydrolyzed in the presence of expensive reagents like silver carbonate or nitrate. Recently, Cushman and co-workers[5] reported a convenient synthetic method for regioselective 1-*O*-acyl hydrolysis of peracylated glycopyranoses with $HgO/HgCl_2$. However, this protocol required highly toxic reagents (HgO and $HgCl_2$) and a prolonged reaction time (2 days). Here we disclose a new synthetic method of 1-hydroxy sugars *via* a regioselective deacylation of peracylated glycopyranoses **1a~d** with $ZnO/ZnCl_2$ system (**Scheme 1**).

Scheme 1



1a~d

2a~d

R^1=Ac, Bz
R^2=OR^1, NHOAc,
R^3=Me, CH_2OR^1

---

*E-mail: orgwyg@css.zju.edu.cn

As shown in **Scheme 1**, we used ZnO/$ZnCl_2$ system as the deacylation reagent. The reaction could smoothly performed in THF-CH_3OH (4:1) under reflux. The optimized reaction time was found to be 3~6 h. A prolonged reaction time resulted in the formation of side-products. The results are summarized in **Table 1**.

Table 1 1-*O*-Deacylation of peracylpyranose

Compd.	R^1	R^2	R^3	Solvents (4:1)	Time (h)	Yield (%)	MS $(M+Na)^+$
2a	Ac	OAc	CH_2OAc	acetone/H_2O	48	63	371.6
2a	Ac	OAc	CH_2OAc	THF/MeOH	6	84	371.6
2b	Bz	OBz	CH_2OBz	acetone/H_2O	48	53	619.3
2b	Bz	OBz	CH_2OBz	THF/ MeOH	6.5	75	619.3
2c	Ac	OAc	Me	THF/ MeOH	4.5	82	313.5
2d	Ac	NHAc	CH_2OAc	THF/ MeOH	3.5	77	370.3

A typical procedure for compound **2a**: To a stirring mixture of 1,2,3,4,6-penta-*O*-acetyl-β -D-glycopyranose (**1a**, 1.56 g, 4 mmol) and ZnO(1.40 g, 17.2 mmol) in THF-MeOH (30 mL:10 mL) was added dropwise a solution of $ZnCl_2$(1.64 g, 12 mmol) in THF(10 mL) at room temperature. The reaction mixture was refluxed for 6 h, then cooled to room temperature, filtered through celite, and concentrated under reduced pressure. The residue was extracted with CH_2Cl_2, washed with aq. $NaHCO_3$ and water, dried over $MgSO_4$. After removing the solvent, the resulting residue was purified by column chromatography on silica gel to give pure **2a** (1.17 g, 84%) as a syrup. ^{1}HNMR (500MHz, $CDCl_3$, δ_{ppm}): 5.55(t, 1H), 5.47(d, 1H, J=3.4Hz), 5.09(t, 1H), 4.91(dd, 1H, J=3.1, 10.2 Hz), 4.27(m, 1H), 4.23(d, 1H, J=4.1 Hz), 4.14(m, 1H), 2.14(s, 3H), 2.11(s, 3H), 2.05(s, 3H), 2.03(s, 3H).

In conclusion, we have developed a facile and efficient method for the preparation of 1-hydroxy-tetra-*O*-acylated glycopyranoses **2** *via* a regioselective deacylation of peracylated glycopyranoses **1** with ZnO/$ZnCl_2$ under mild conditions.

References

1. H. Paulsen, *Angew. Chem., Int. Ed. Engl.*, **1990**, *29*, 823.
2. F. Barresi, O. Hindsgaul, *J. Carbonhydr. Chem.*, **1995**, *14*, 1043.
3. R. R. Schmidt, W. Kinzy, *Adv. Carbohydr. Chem. Biochem.*, **1994**, *50*, 21. and references therein.
4. (a) O. T. Schmidt, J. Herok, *Liebigs Ann. Chem.*, **1954**, *587*, 63. (b) W. A. Bonner, *J. Am. Chem. Soc.*, **1958**, *80*, 3372.
5. T. Sambaiah, P. E. Fanwick, M. Cushman, *Synthesis*, **2001**, *10*, 1450.

Received 29 April, 2002