

Microwave-assisted Regioselective 1-*O*-Deacylation of Peracylated Glycopyranoses on Alumina

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Abstract: A facile, rapid and regioselective method for the 1-*O*-deacylation of peracylated glycopyranoses is described which occurs under mild conditions by absorption onto alumina using microwave irradiation.

Keywords: Deacylation, sugars, regioselectivity, microwave irradiation.

Suitably 1-hydroxy sugars are important materials and valuable building blocks for the preparation of various glycosyl donors¹⁻³ in the synthesis of oligosaccharides and glycoconjugates. During the decades, several methods for preparing 1-OH peracylated pyranoses have been established, which involve hydrolysis of acylglycosyl halides⁴ or thioglycosides⁵ and regioselective deacetylation at the anomeric position⁶. But these protocols still have some drawbacks such as highly basic conditions, prolonged reaction time, side product formation, poisonous or expensive reagents and need of two-step reaction procedure. Previously, we have reported a facile approach for regioselective 1-*O*-acyl hydrolysis of peracylated glycopyranoses with ZnO/ZnCl₂ using THF-CH₃OH as solvents⁷, however it also required a prolonged reaction time.

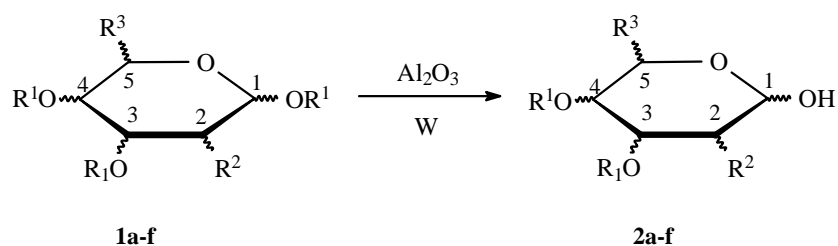
Microwave technology has been applied beneficially into a number of organic reactions⁸. The microwave assisted hydrolysis of esters is well-known but the regioselective hydrolysis of esters at the anomeric position in sugars under this condition has not been described. In the course of our study on carbohydrate chemistry, we found that microwave irradiation could promote the regioselective deacylation of peracylated glycopyranoses **1** to give the corresponding 1-OH derivatives **2** in moderate yields (**Scheme 1**). Here, we wish to report our primary experiment results.

Initially, we investigated the effect of microwave irradiation on the *O*-deacylation of 1, 2, 3, 4, 6-penta-*O*-acetyl-D-glucopyranose **1a** and found that reaction gave the 1-*O*-deacetylated product **2a** in the yield of 67%, which took place regioselectively without any group migration. This result prompted us to examine other fully acylated sugars. Thus, 1, 2, 3, 4, 6-penta-*O*-benzoyl-D-glucopyranose **1b**, 1, 2, 3, 4-tetra-*O*-acetyl-L-rhamnopyranose **1c**, 1, 2, 3, 4-tetra-*O*-benzoyl-L-rhamnopyranose **1d**, acetamido-

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2-deoxy-1, **1d**, acetamido-2-deoxy-1, **1d**, acetamido-2-deoxy-1, 3, 4, 6-tetra-*O*-acetyl-D-glucopyranose **1e** and 1, 2, 3, 4-tetra-*O*-acetyl-D-arab--inopyranose **1f** afforded corresponding 1-OH sugar derivatives **2b-2f**⁹. As shown in **Table 1**, the reaction could complete in 5-10 min. To prolong the reaction could not improve the yield.

Scheme 1

**Table 1** O-Deacylation of Peracylpyranose

Compd.	R ¹	R ²	R ³	Time (min)	Yield (%)	MS (M+Na) ⁺
2a	Ac	OAc	CH ₂ OAc	7	67	371.5
2b	Bz	OBz	CH ₂ OBz	8	54	619.5
2c	Ac	OAc	Me	6.5	65	313.3
2d	Bz	OBz	Me	7.5	56	499.5
2e	Ac	NHAc	CH ₂ OAc	10	60	370.3
2f	Ac	OAc	H	6.5	64	299.5

A typical procedure for compound **2f**: Neutral alumina¹⁰ (5.0 g) was added to a solution of 1,2,3,4-tetra-*O*-acetyl-D-arabinopyranose **1f** (0.318 g, 1 mmol) in CH₂Cl₂ (1-2 mL) at room temperature and mixed thoroughly. The air-dried mixture was placed in a small beaker and irradiated in a microwave oven¹¹. The reaction was monitored by TLC until it was completed. The product was extracted with CH₂Cl₂ (4×15 mL). After removal of the solvent under reduced pressure, the residue was purified through a silica gel column to give **2f** (0.177 g, 64%) as a yellow syrup. ESI-MS: *m/z* = 299.5 (M+Na)⁺; ¹HNMR (500 MHz, CDCl₃, δ_{ppm}): 5.48 (d, 0.7H, J=3.2 Hz, H-1), 5.41 (dd, 1H, J=3.4 and 10.5 Hz, H-4), 5.33 (brs, 1H, OH), 5.27 (d, 0.3H, J=7.3 Hz, H-1), 5.20 (dd, 1H, J=3.3 and 10.9 Hz, H-2), 5.09 (m, 1H, H-3), 4.21 (dd, 1H, J=5.9 and 12.3 Hz, H-5a), 3.71 (m, 1H, H-5b), 2.18 (s, 3H, COCH₃), 2.13 (s, 3H, COCH₃), 2.03 (s, 3H, COCH₃).

In conclusion, we have developed a facile and rapid method for the regioselective 1-*O*-deacylation of peracylated glycopyranoses by hydrolysis on inexpensive neutral alumina assisted by microwave irradiation.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (No. 20272051).

References and Notes

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9. The analytic data of compounds **2a-2e** have been submitted to the editorial office of CCL.
10. Neutral Aluminium oxide [for chromatography use] (shanghai xin cheng fine chemical co.LTD) was used as received.
11. A Galanz microwave oven (model WP700, Galanz Co. Shunde, China) with adjustable power level , at full power (700W), was used for microwave irradiation.

Received 19 September, 2002