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Note

An Alternative Method for Anomeric Deacetylation of Per-acetylated Carbohydrates

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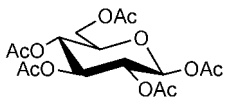
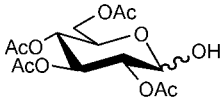
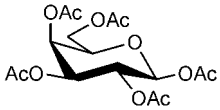
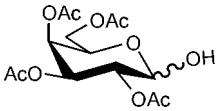
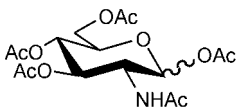
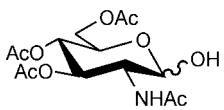
An alternative method for anomeric deacetylation of fully acetylated carbohydrates has been developed using imidazole in methanol.

Keywords acetylated 1-hydroxy sugar, anomeric deacetylation, imidazole

Suitably protected 1-hydroxy sugars, especially the acetylated 1-hydroxy sugars, are valuable building blocks for the construction of various glycosyl donors, which are widely used for glycosylation reactions in carbohydrate chemistry.[1-5] Except for hydrolysis of scare glycosyl halide,[6] the acetylated 1-hydroxy sugars are usually prepared by anomeric deacetylation of fully acetylated derivatives with basic or acidic reagents, such as hydrazine hydrate,[7] hydrazine acetate,[8] 2-aminoethanol,[9] piperidine,[10] ammonia,[11,12] butylamine,[13] dimethylamine,[13] benzylamine,[14] ethylenediamine,[15] potassium hydroxide,[16] potassium cyanide,[16] potassium carbonate,[17] sodium methoxide,[18] stannic tetrachloride,[19] hydrogen bromide,[20] trifluoroacetic acid,[21] guanidine,[22] piperidinium acetate,[23] ammonium carbonate,[24] tributyltin methoxide or bisbutyltin oxide,[16] Enzymes,[25] and silica gel.[26] Recently, Sambaiah *et al*.[27] has reported a convenient method for regioselective 1-*O*-acyl hydrolysis of peracylated glycopyranose at neutral pH using mercuric chloride and mercuric oxide. Most reagents above-described are either highly toxic or corrosive. In addition, the rate of the anomeric deacetylation varies depending both on the anomeric configuration of the starting sugar and the nature of substituent present. Therefore, it is useful to have a large choice of reagents applicable for this purpose in various situations. Herein, we report an alternative method for anomeric deacetylation of fully acetylated carbohydrates using imidazole in methanol at 40 ℃, and the results are summarized in Table 1. In the case of yield alone, our method has no clear advantage over the reported procedures, but the reagent empolyed in our method, imidazole, is a very conveniently measured solid material with relatively low toxicity, readily commercially available and cheap. And this method does not require anhydrous conditions. Compared with previously reported methods, it is operationally simple, economical and practical.

Table 1 Regioselective anomeric deacetylation of fully acetylated carbohydrates

Entry	Substrate	Product[a]	Yield[b]/%	Reaction time/h
1			63.1	29
2			68.4	32
3			82.3	24

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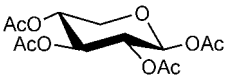
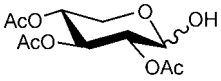
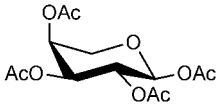
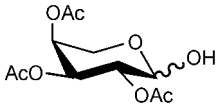
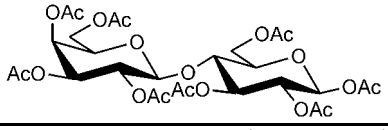
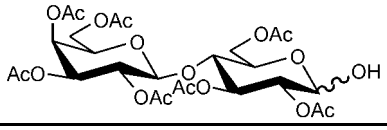
Continued

Entry	Substrate	Product[a]	Yield[b]/%	Reaction time/h
4			72.1	28
5			76.2	31
6			60.7	34

[a] All compounds were comfirmed by ^{1}H NMR and ^{1}H-^{1}H Cosy. [b] Isolated yield by chromatography.

General procedure for anomeric deacetylation

To a solution or suspension of fully acetylated sugars (1 mmol) in 15 mL of methanol was added imidazole (1 mmol), and the mixture was stirred at 40 ℃ until TLC showed that almost absence of starting material and presence of a product, in most cases, appeared as two poorly separated spots representing a mixture of anomers. Then the mixture was evaporated under reduced pressure to obtain yellowish viscous residue, which was subjected to chromatography to afford the desired products.

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