



Note

Trichloroisocyanuric acid (TCCA): an efficient green reagent for activation of thioglycosides toward hydrolysis



Nabamita Basu, Sajal Kumar Maity, Aritra Chaudhury, Rina Ghosh *

Department of Chemistry, Jadavpur University, Kolkata 700 032, India

ARTICLE INFO

Article history:

Received 21 November 2012

Received in revised form 31 December 2012

Accepted 2 January 2013

Available online 9 January 2013

Keyword:

Thioglycosides

Trichloroisocyanuric acid

Hemiacetals

TCCA

Hydrolysis

ABSTRACT

Trichloroisocyanuric acid (TCCA), an inexpensive, commercially available, and non-toxic reagent has been used for the activation of thioglycosides toward their hydrolysis to the corresponding hemiacetals in high to excellent yields. The methodology provides a mild reaction condition for dealing with compounds containing acid sensitive functional groups.

© 2013 Elsevier Ltd. All rights reserved.

A careful choice of anomeric protecting group is always an important part of planning strategy for synthesizing complex oligosaccharides. Moreover, sometimes it is necessary to remove the anomeric protecting group selectively or it is required to transform it to an activated glycosyl donor for further glycosylation toward the assembly of complex oligosaccharides.¹ Protected 1-hydroxy sugars can be synthesized from (a) glycosyl acetates by using hazardous hydrazine hydrate² or by organic bases like benzylamine or *tert*-butyl amine,³ (b) alkyl glycosides by hydrolysis of glycosidic bond under acidic conditions,⁴ or (c) by hydrolysis of thioglycosides. Of which, the hydrolysis of thioglycosides is more convenient as it opens the way for getting glycosyl hemiacetals having diverse functionalities under mild conditions. Therefore, hydrolysis of thioglycosides is the first choice to chemists for preparing glycosyl hemiacetals which can further be converted into more reactive glycosyl donors such as trichloroacetamide,⁵ fluoride,⁶ or can also be used as such in dehydrative glycosylation reaction.⁷ Moreover, glycosyl hemiacetals have been successfully used as synthons for the chiral synthesis of optically pure natural products or for preparation of azasugars.⁸

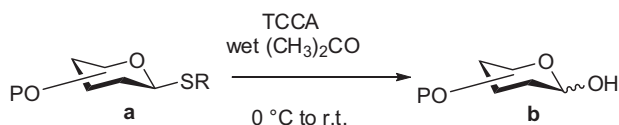
To date, a number of methods have been reported for hydrolysis of thioglycosides, which include use of toxic thiophilic heavy metals, NIS in wet acetone, or in the presence of acid (TfOH⁹ or TFA¹⁰), NBS,¹¹ V₂O₅/H₂O₂/NH₄Br,¹² (NH₄)₆Mo₇O₂₄/H₂O₂–HClO₄/NH₄Br,¹³ Bu₄NIO₄/HClO₄,¹⁴ or Bu₄NIO₄/TfOH,¹⁴ chloramine-T,¹⁵ and N-iodosaccharine.¹⁶ However, some of these suffer from limitations such

as, use of expensive or toxic reagent,² incompatibility of acid-susceptible group present in the carbohydrate substrates, harsh reaction condition, lower yields, etc. Thus, exploration of other efficient reagents and metal-free conditions toward this end is worth pursuing. Trichloroisocyanuric acid (TCCA),¹⁷ a commercially available, inexpensive, and non-toxic reagent, used in various organic syntheses is known to be a chlorinating agent too. Very recently, we have successfully used TCCA in the glycosylation reaction using both armed and disarmed donors.¹⁸ Its low pK_a (1.8) and high active chlorine content (91.5%)¹⁷ indicate it to be an efficient chloronium ion generator, and thus is expected to activate thioglycoside to react with good nucleophiles without the requirement of any other strong acids as co-activator. Our proposition was eventually proved, as a model thioglycoside (**1a**) was hydrolyzed in the presence of TCCA at ambient temperature. Avoiding the use of strong acid as co-activator could make this method more attractive for hydrolyzing thioglycosides owing to the survival of acid-labile protecting groups present in carbohydrate derivatives. As a part of our ongoing research to prepare hemiacetals for the synthesis of diverse materials, we are pleased to report herein, hydrolysis of thioglycosides activated by TCCA, and the results are summarized in Schemes 1 and 2 and Tables 1–3. To the best of our knowledge, this is the first report of thioglycoside hydrolysis by TCCA.

At the outset, the reaction condition was standardized from a set of few reactions of **1a** done under different conditions (Table 1). Under the standard condition **1a** reacted in aqueous acetone (1:4) at ambient temperature in the presence of TCCA (1 equiv) generating the corresponding hemiacetal (**1b**) in excellent yield (Table 1, entry 3).

* Corresponding author. Fax: +91 033 2414 6266.

E-mail addresses: ghoshrina@yahoo.com, ghosh_rina@hotmail.com (R. Ghosh).



Scheme 1. TCCA mediated conversion of thioglycoside to the corresponding hemiacetal.

Then the efficiency of this procedure was compared with some reported reagents using **1a** as the starting material. Though other reagents furnished **1b** in high yields, the best result was obtained with TCCA (**Table 2**, entry 1).

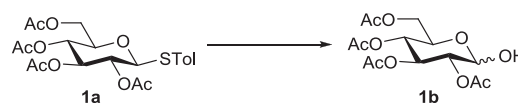
After the success of the initial reaction we turned our attention to the evaluation of the hydrolyzing capability of TCCA on a series of thioglycoside derivatives. A variety of other thioglycosides (**Fig. 1**) bearing OAc, OBz, OBn, Npht, acetal, etc. protecting groups reacted under the standard protocol to produce the corresponding hemiacetals in high to excellent yields (**Table 3**). In no case, formation of trace of sugar-isocyanuric acid adduct could be detected.

Glucose, galactose, and mannose based ester and ether protected thioglycosides (entries 1, 2, 4, 5, 6, 7, 9, 10, and 11) were hydrolyzed within 30 min resulting in the desired products in excellent yields (85–97%, **Table 3**). Acid labile benzylidene protecting groups in the substrates (entries 3 and 8) remained unaffected during the course of reaction, and no decomposition was observed, thus the corresponding hemiacetal products (**3b** and **8b**) were obtained in excellent yields. Benzylidene and ester protected glucosamine donors (entries 15–17) needed longer reaction time (1 h) for completion of hydrolysis to furnish the corresponding hemiacetals (**14b–16b**). Fuco- (entry 13) and rhamno- (entry 12) thioglycosides also took longer reaction time (1 h) for completion of reactions; the resulting products were obtained in high yields (85–87%, **Table 3**). Hydrolysis of perbenzylated thiofucose (**13a**) was complete in 30 min to give **13b** in 94% yield (entry 14). Cellobiose, lactose, and maltose derived thioglycoside donors produced the corresponding hemiacetals (**17b–19b**, entries 18–20) in excellent yields (91–95%) within an hour. Differentially protected disaccharide based thioglycoside (**20a**²⁵) generated from D-glucosamine took 2 h to afford the corresponding hydrolyzed product (**20b**) in 86% yield. Finally the efficiency of this methodology was again established by hydrolysis of **2a**, **3a** and **11a** under a scale-up condition (~20 times, 2 g scale, entries 2, 3 and 12, under parentheses, **Table 3**), which generated the corresponding products in excellent yields (89–96%).

This reaction is supposed to proceed following the pathway as shown in **Scheme 2**.

In summary TCCA has been utilized as a commercially available, non-toxic, inexpensive, and green reagent for efficient hydrolysis

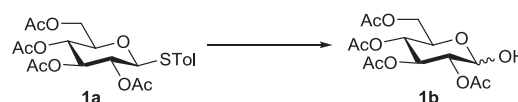
Table 1
Standardization of solvent and reagent load



Entry	Solvent	TCCA (equiv)	Yield ^a (%)
1	(CH ₃) ₂ CO/H ₂ O (9:1)	0.5	81
2	(CH ₃) ₂ CO/H ₂ O (9:1)	1.0	92
3	(CH ₃) ₂ CO/H ₂ O (9:1)	1.0	97
4	CH ₃ CN/H ₂ O (9:1)	1.0	90
5	CH ₃ Cl ₂ /H ₂ O (9:1)	1.0	87

^a Chromatographed yield.

Table 2
Hydrolysis of thioglycoside (**1a**) using different reagents



Entry	Solvent	mmol/1 mmol 1a	Yield ^a (%)
1	TCCA	1.0	97
2	NIS/H ₂ SO ₄ -Silica ¹⁹	1.2/100 mg	90
3	N-Iodosaccharin ¹⁶	1.5	95
4	NIS/TFA ¹⁰	1.0/1.0	88
5	NIS/TfOH ⁹	1.5/0.10	90
6	NBS ¹¹	2.0	90
7	NBS/CaCO ₃ ²⁰	2.0/5.0	87

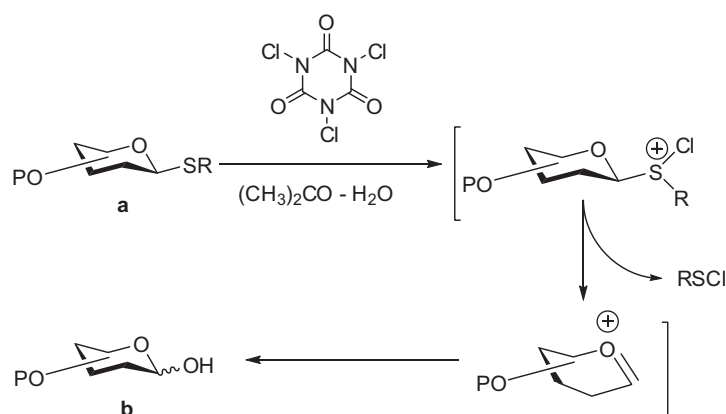
^a Chromatographed yield.

of thioglycosides under mild condition. A variety of commonly used, acid labile protecting groups remain unaffected in the presence of this reagent.

1. Experimental section

1.1. General

Petroleum ether (PE, 60–80 °C) was used for chromatographic purpose. Flash column chromatography was performed on Silica



Scheme 2. Plausible mechanism for thioglycoside hydrolysis.

Download English Version:

<https://daneshyari.com/en/article/1387712>

Download Persian Version:

<https://daneshyari.com/article/1387712>

[Daneshyari.com](https://daneshyari.com)