Chinese Chemical Letters 25 (2014) 561–566

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

$SrCl_2$ as an efficient cocatalyst for acidic hydrolysis of methyl glycosides

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ARTICLE INFO

Article history:
Received 8 October 2013
Received in revised form 23 October 2013
Accepted 12 November 2013
Available online 21 November 2013

Keywords:
Cocatalyst
Hydrolysis
Lewis acid
Methyl glycoside
Strontium chloride

ABSTRACT

$SrCl_2$ was found to be the most efficient cocatalyst for the acidic hydrolysis of methyl glycosides after 26 kinds of most representative metal salts were screened. The $SrCl_2$-cocatalyzed acidic hydrolysis of methyl glycosides is highlighted by short reaction times, less byproducts and high yields. A possible mechanism for the $SrCl_2$-cocatalyzed hydrolysis is also proposed.

1. Introduction

Methyl glycosides constitute an important class of carbohydrate derivatives. Their hydrolysis can produce the corresponding lactols, which are important intermediates for further modifications [1] or can be used to prepare glycosyl donors for the construction of oligosaccharides [2–4].

Hydrolysis of methyl glycosides to their corresponding lactols is always carried out under rather harsh conditions [5–13], which are characterized by strongly acidic reaction media and high reaction temperatures [5–8], and often suffers from poor yields [9–12] and large quantities of byproducts which can cause great trouble in purification in many cases [12,13]. Survey of literature revealed that there are no currently available methods to solve these problems. Prompted by these unsolved shortcomings in the current methods, we were interested in finding a cocatalyst to promote the hydrolysis while suppressing the formation of byproducts so that relatively mild hydrolysis conditions could be adopted and the aforementioned drawbacks could be solved. Considering the fact that when methyl glycosides are ready for acidic hydrolysis their hydroxyl groups are usually protected by robust protecting groups, such as alkyl and benzyl groups [5–13], because most other protecting groups usually cannot survive the harsh hydrolysis conditions, we chose the methyl glycosides with methyl and benzyl protecting groups for our study (Fig. 1). We herein report an efficient cocatalyst, $SrCl_2$, for the acidic hydrolysis of methyl glycosides, which can be highlighted as inexpensive, shortening reaction times, suppressing formation of byproducts and improving yields.

2. Experimental

The melting points were measured with an XT-4 microscopic melting apparatus and are uncorrected. The ^1H NMR spectra were recorded on a Bruker AV400 spectrometer with DMSO-d_6 as solvent and TMS as internal standard. HPLC analyses were performed with a Waters 2695 high-performance liquid chromatograph equipped with a Diamonsil C_8 column (150 mm × 4.6 mm, 5 μm; held at 35 °C) and a UV detector (210 nm), using MeCN/H_2O (90/10, v/v) as mobile phase at a flow rate of 0.6 mL/min.

Methyl tetra-*O*-benzylglycosides **1**–**6** were prepared from their corresponding unprotected methyl glycosides following a known one-step procedure [14]. Compounds **7** and **8** were prepared from methyl α-D-glucopyranoside following known procedures [15,16], and substrate **9** was prepared according to a known method [1]. All

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http://dx.doi.org/10.1016/j.cclet.2013.11.028

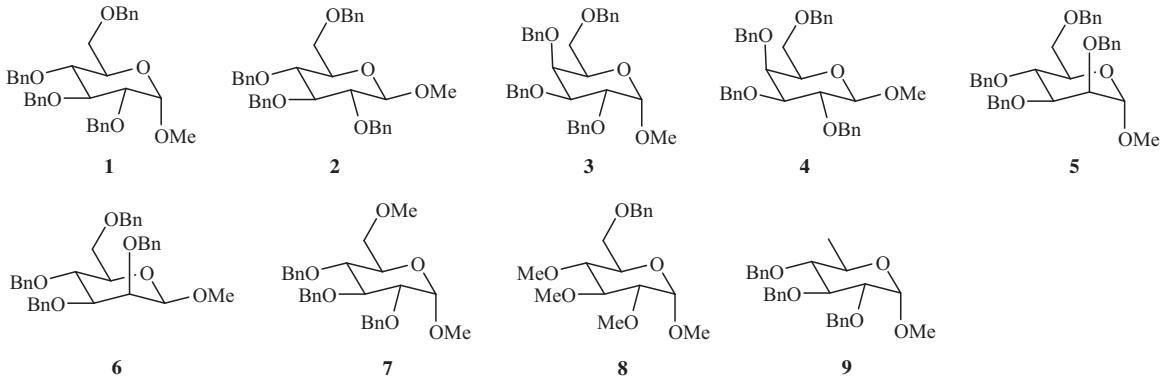


Fig. 1. Substrates used for the $SrCl_2$-cocatalyzed acidic hydrolysis.

the substrates **1–8** are known compounds and their melting points or ^{1}H NMR data were in good agreement with those reported.

Procedure for screening of concentration of HCl and reaction temperature: In a 50 mL round-bottomed flask, 1.00 g (1.8 mmol) of **1** was dissolved in 6 mL of glacial acetic acid, and the solution was stirred and heated to a specific temperature (Table 1). To the mixture was added 1 mL of HCl with a specific concentration (Table 1). The reaction was timed just after the addition of HCl, and aliquots of the reaction mixture were subjected to HPLC analysis at 30 min intervals to follow the reaction course until a conversion of >95% was reached.

Procedure for screening of the kind of metal salt: In a 50 mL round-bottomed flask, 1.00 g (1.8 mmol) of **1** was dissolved in 6 mL of glacial acetic acid, and the solution was stirred and heated to 70 °C. To the mixture was added 1 mL of 5 mol/L HCl, followed by addition of 1.0 eq. of metal salt (Table 2). The reaction was timed just after the addition of HCl and metal salt, and aliquots of the reaction mixture were subjected to HPLC analysis at 30 min intervals to follow the reaction course until a conversion of >95% was reached.

Procedure for screening of equivalent of metal salt: In a 50 mL round-bottomed flask, 1.00 g (1.8 mmol) of **1** was dissolved in 6 mL of glacial acetic acid, and the solution was stirred and heated to 70 °C. To the mixture was added 1 mL of 5 mol/L HCl, followed by addition of a specific equivalent of metal salt (Table 3). The reaction was timed just after the addition of HCl and metal salt, and aliquots of the reaction mixture were subjected to HPLC analysis at 30 min intervals to follow the reaction course until a conversion of >95% was reached.

Table 1
Results for screening of HCl concentration and reaction temperature using **1** as substrate[a].

Entry	HCl (mol/L)[a]	Temperature (°C)	Time (min)[b]
1	6	80	90
2	6	70	240
3	6	60	420
4	5	80	120
5	5	70	390
6	5	60	720
7	4	80	150
8	4	70	420
9	4	60	>720
10	3	80	240
11	3	70	660
12	3	60	>720
13	2	80	390
14	2	70	>720
15	2	60	>720

[a] Reaction conditions: 1.00 g of **1**, 1 mL of HCl, 6 mL of AcOH.
[b] Reaction times corresponding to 95% conversion were measured by HPLC analysis (C_8 column, 210 nm, MeCN/H_2O = 90/10 (v/v)).

Procedure for acidic hydrolysis of **1–9** to test the generality of $SrCl_2$ as cocatalyst: In a 50 mL round-bottomed flask, 1.00 g of substrate **1–9** was dissolved in 6 mL of glacial acetic acid, and the solution stirred and heated to 70 °C (Table 4). To the mixture was added 1 mL of 5 mol/L HCl, followed by the addition of 0.10 eq. of $SrCl_2{\cdot}6H_2O$. The reaction was timed just after the addition of HCl and $SrCl_2{\cdot}6H_2O$, and aliquots of reaction mixture subjected to HPLC analysis at 30 min intervals to follow the reaction course until a conversion of >95% was reached. The reaction mixture was quenched by adding 50 mL of ice-water, and the resulting mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and evaporated on a rotary evaporator to afford the crude lactols, which were purified by column chromatography to yield the pure lactols **10–15**. All the lactols **10–15** corresponding to **1–9** are known compounds, and their melting points or ^{1}H NMR were in good agreement with those reported (Table 4).

3. Results and discussion

The corresponding lactols produced by hydrolysis of methyl glycosides are versatile intermediates in organic chemistry (Scheme 1). According to our earlier study [1] and the report of Koto *et al.* [12], the hydrolysis of methyl glycosides needed rather harsh reaction conditions, most of which involved heating the methyl glycosides in glacial acetic acid at high temperatures with aqueous strong acids, such as H_2SO_4 [10,11], HCl [7,8,12] and TfOH [6]. These harsh reaction conditions could indeed result in quick reactions; however, a main drawback was that the desired product often included large quantities of byproducts, such as debenzylated products [12,13], complicating the workup and purification procedures and resulting, in many cases, in poor yields [9–12] due notably to the reaction conditions [12] (Scheme 2). In the normal acidic hydrolysis of methyl glycosides, the protons chelate the glycosidic oxygen atoms aiding the cleavage of the glycosidic bond. Since metal ions are also electron-deficient species which can also chelate these oxygen atoms in an identical way to protons, selection of a metal salt as a Lewis acid cocatalyst to accelerate the hydrolysis step while suppressing the formation of byproducts was desired to solve the problems in the reported methods associated with the hydrolysis of methyl glycosides.

With high concentrations of HCl and high temperatures, the acidic hydrolysis of methyl glycosides can proceed quickly, but often leads to large quantities of byproducts and poor yields [12]. So, *prior to* the screening of metal salts as cocatalysts, suitable reaction conditions to complete the hydrolysis of methyl glyco-

Table 2
Results for screening of metal salts as cocatalyst using **1** as substrate.

Entry	Metal salt[a]	Time (min)[b]	Yield (%)[c]	Purity (%)[d]	Number of impurities
1	LiCl	240	73	85	4
2	NaCl	240	71	84	4
3	KCl	240	70	82	6
4	RbCl	240	73	84	3
5	CsCl	540	74	81	4
6	$MgCl_2$	300	82	87	2
7	$CaCl_2$	210	77	83	4
8	$BaCl_2$	300	81	87	3
9	$SrCl_2$	210	90	94	2
10	$AlCl_3$	210	55	67	9
11	$ZnCl_2$	180	60	71	9
12	$SnCl_2$	420	71	83	5
13	$SnCl_4$	240	52	66	9
14	$CdCl_2$	210	69	78	5
15	$HgCl_2$	210	73	81	5
16	$PbCl_2$	270	73	84	4
17	$BiCl_3$	180	66	76	7
18	$TiCl_4$	120	51	66	9
19	$CrCl_3$	390	75	84	4
20	$MnCl_2$	210	88	92	2
21	$FeCl_3$	270	77	86	4
22	$CoCl_2$	360	85	90	2
23	$NiCl_2$	270	83	89	2
24	$CuCl_2$	150	85	91	2
25	$Ce_2(SO_4)_3$	330	81	88	3
26	$Ce(SO_4)_2$	240	68	79	6

[a] 1.0 eq. of metal salt was used. Some metal salts used were in their hydrated forms: $MgCl_2·6H_2O$, $BaCl_2·2H_2O$, $SrCl_2·6H_2O$, $SnCl_2·2H_2O$, $SnCl_4·6H_2O$, $CrCl_3·6H_2O$, $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $CuCl_2·2H_2O$, $Ce_2(SO_4)_3·8H_2O$, and $Ce(SO_4)_2·4H_2O$.
[b] Reaction times corresponding to 95% conversion were measured by HPLC analysis (C_8 column, 210 nm, MeCN/H_2O = 90/10, v/v).
[c] Yields of the desired product **10** were measured by HPLC analysis under conditions described above.
[d] The purity of **10** herein was reflected by the purity of **10** in the crude reaction mixture determined by HPLC under conditions described above.

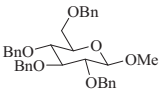
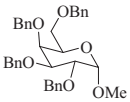
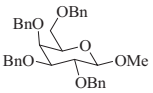
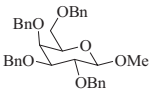
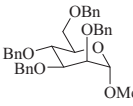
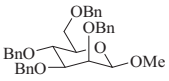
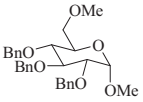
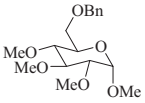
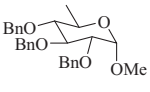
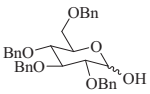
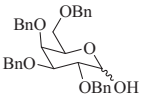
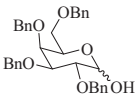
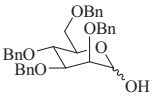
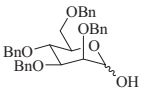
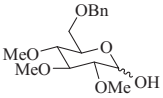
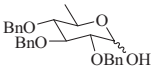
sides within a reasonable time should be found because if the hydrolysis rate proceeds too fast or too slow, it will be difficult to clearly detect the effect of the cocatalysts. We chose the commonly encountered methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **1** (Scheme 2) as the substrate for the initial screening of the two important hydrolysis parameters, *i.e.* the concentration of the acid and the reaction temperature. It should be noted that HCl, as the acid, and metal chlorides, as the Lewis acid cocatalyst, were used throughout our study because most metal chlorides are soluble in water whereas many of their sulfate counterparts are not. The results are shown in Table 1. The concentration of HCl ranged from 2 mol/L to 6 mol/L, and the reaction temperatures ranged from

Table 3
Results for screening of equivalent of cocatalysts using **1** as substrate.

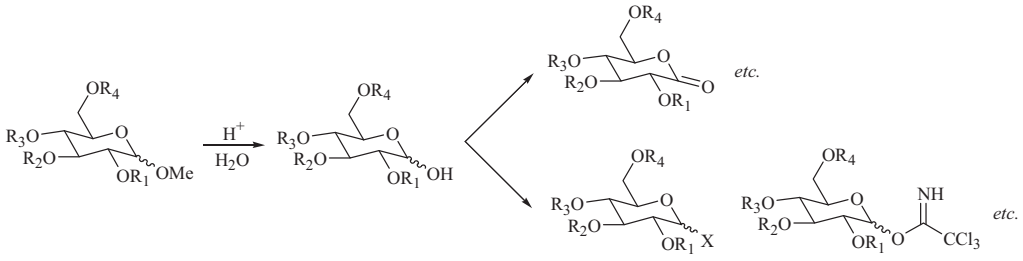
Entry	Metal salt[a]	Quantity (eq.)[b]	Time (min[c]	Yield (%)[d]	Purity (%)[e]	Number of impurities
1	$SrCl_2$	0.01	240	71	81	6
2	$SrCl_2$	0.05	210	77	84	4
3	$SrCl_2$	0.1	150	91	95	2
4	$SrCl_2$	0.2	150	90	92	2
5	$SrCl_2$	0.4	150	90	93	2
6	$SrCl_2$	0.8	180	89	92	2
7	$SrCl_2$	1.0	210	90	94	2
8	$SrCl_2$	2.0	240	88	91	2
9	$MnCl_2$	0.01	300	70	82	4
10	$MnCl_2$	0.05	270	70	83	4
11	$MnCl_2$	0.1	270	73	86	3
12	$MnCl_2$	0.2	240	78	84	3
13	$MnCl_2$	0.4	240	80	87	2
14	$MnCl_2$	0.8	210	82	88	2
15	$MnCl_2$	1.0	210	88	92	2
16	$MnCl_2$	2.0	240	76	84	3
17	$CuCl_2$	0.01	210	82	90	2
18	$CuCl_2$	0.05	180	84	90	2
19	$CuCl_2$	0.1	180	83	89	2
20	$CuCl_2$	0.2	150	80	86	3
21	$CuCl_2$	0.4	150	82	88	3
22	$CuCl_2$	0.8	150	84	90	2
23	$CuCl_2$	1.0	150	85	91	2
24	$CuCl_2$	2.0	150	81	87	3

[a] Some metal salts used were in the hydrated forms: $SrCl_2·6H_2O$ and $CuCl_2·2H_2O$.
[b] The quantities were based on the substrate **1**.
[c] Reaction times corresponding to 95% conversion were measured by HPLC analysis (C_8 column, 210 nm, MeCN/H_2O = 90/10, v/v).
[d] Yields of the desired product **10** were measured by HPLC analysis under conditions described above.
[e] Purity of **10** was herein reflected by the purity of **10** in the crude reaction mixture as determined by HPLC under conditions described above.

Table 4
Hydrolysis of a variety of methyl glycosides **2**–**9** with 0.1 eq. of $SrCl_2$ under optimized reaction condition.

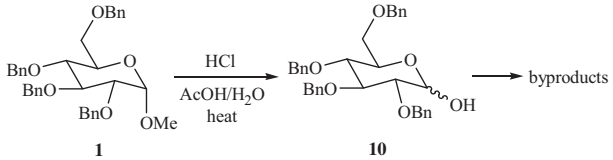
Entry	Substrate	Product	Reaction time (min)[a]	Yield (%)[b]	Identification [c]
1			120	90	White solid. M.p. 150–151 °C (lit. [17] 150–152 °C)
2			60	88	Oil. ^{1}H NMR data were in agreement with those reported [18]
3			60	89	Oil. ^{1}H NMR data were in agreement with those reported [18]
4			150	91	Oil. ^{1}H NMR data were in agreement with those reported [19]
5			150	90	Oil. ^{1}H NMR data were in agreement with those reported [19]
6			150	92	White solid. M.p. 128–129 °C. ^{1}H NMR data were in agreement with those reported [20]
7			180	87	Oil. ^{1}H NMR data were in agreement with those reported [16]
8			90	92	White solid. M.p. 92–94 °C (lit. [1] 92–94 °C)

[a] Reaction times corresponding to 95% conversion were measured by HPLC analysis (C_8 column, 210 nm, MeCN/H_2O = 90/10, v/v).
[b] Isolated yields.
[c] Structural confirmation of the products. Melting points or ^{1}H NMR spectra of the products were compared with those reported.



Scheme 1. Examples for hydrolysis of methyl glycosides and the representative applications of lactols thus produced.

60 °C to 80 °C. As can be observed clearly in Table 1, the reaction rate responded much more dramatically to the temperature change than to the change of HCl concentration. The reaction rate decreased significantly below 70 °C and increased quickly above



Scheme 2. Hydrolysis of **1** to its corresponding lactol **10** and the formation of byproducts that follows.

70 °C, therefore, 70 °C was selected as the optimum temperature. At 70 °C, the reaction times ranged from 240 min to >720 min, and finally 390 min was believed to the optimum reaction time at 5 mol/L of HCl and most suitable for further screening of metal salts as cocatalyst (entry 5 in Table 1).

With in hand the optimum conditions for the screening of metal salts, *i.e.* 5 mol/L HCl at 70 °C, we proceeded to screen 26 representative metal salts as cocatalyst using **1** as substrate (Table 2). As shown in Table 2, with soft alkali metal ions (entries 1–5) the hydrolysis exhibited a slight improvement compared with that without any metal salt (entry 5 in Table 1); however, they were marked by longer reaction times and moderate yields and impurity profiles. The hard metal ions (entries 10, 11, 13, 17, 18

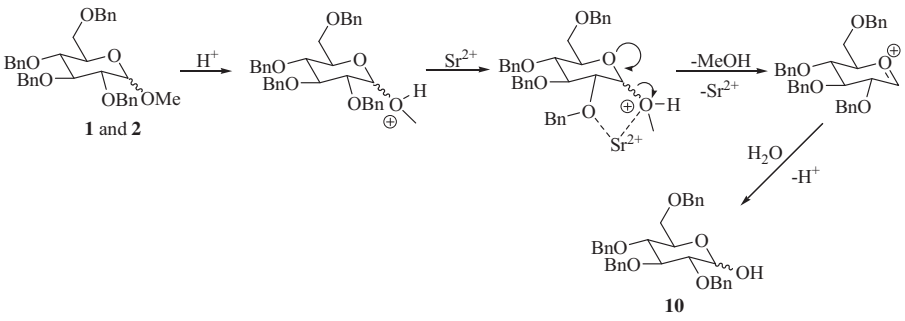


Fig. 2. Proposed mechanism of $SrCl_2$-cocatalyzed hydrolysis exemplified by **1** and **2**.

and 26) could considerably accelerate the reaction, but, unfortunately, could lead to the formation of significant levels of byproducts, and dramatically decreased yields. Based on the comprehensive evaluation in terms of reaction time, yield and purity, three metal salts, $SrCl_2$ (entry 9), $MnCl_2$ (entry 20) and $CuCl_2$ (entry 24), were selected for further investigation and indicated that moderate hardness of the metal ions is best suited for the our purpose. Neither too soft nor too hard metal ions were appropriate for the hydrolysis, with the former ones having insufficient cocatalytic efficiency while the latter ones exhibiting too powerful cocatalytic efficiency that led to decomposition of the products as well.

Since the preliminary screenings used 1.0 eq. of metal salts as shown in Table 2, we determined to study the effect of the quantity of the cocatalyst on the cocatalytic efficiency (Table 3). The reactions were carried out with the three designated metal salts using **1** as substrate and optimum reaction conditions, *i.e.* 5 mol/L HCl at 70 °C. As shown in Table 3, as the quantity of cocatalyst increased, the reaction rates with all three cocatalysts gradually increased to reach plateaus. The reaction rate with $SrCl_2$ and $MnCl_2$ also displayed slight decreases at specific large quantities (entries 8 and 16). The smallest quantities of these three cocatalysts corresponding to the best reaction rates were then determined as 0.1 eq. for $SrCl_2$, 0.8 eq. for $MnCl_2$, and 0.2 eq. for $CuCl_2$. Further examination of the data found that 0.1 eq. of $SrCl_2$ was the best because it corresponded to the shortest reaction time (150 min) and highest yield (91%) and impurity profile (95% with 2 impurities). So, $SrCl_2$ was finally selected as the best cocatalyst for use at a low concentration of 0.1 eq.

With in hand the best cocatalyst and its quantity (0.1 eq. of $SrCl_2$) under the optimum reaction conditions (5 mol/L HCl at 70 °C) established, we tested the generality of this cocatalyst with a variety of methyl glycosides as the substrate (Table 4). As shown in Table 4, when substrates **2**–**9** were subjected to the acidic hydrolysis cocatalyzed by 0.1 eq. of $SrCl_2$ and optimizes conditions, the reactions all proceeded very well, completing within short reaction times and furnishing the corresponding lactols in good yields. The results demonstrated that $SrCl_2$ can be used as an efficient cocatalyst for the acidic hydrolysis of methyl glycosides.

The mechanism for the cocatalysis with $SrCl_2$ is postulated as proceeding *via* the bidentate chelation of the glycosidic and 2-*O* atoms to the Sr^{2+} ion, forming a 5-membered ring which facilitated the acidic hydrolysis that followed (Fig. 2). The 5-membered ring intermediate is consistent to a similar process reported earlier [21]. As can be clearly shown in Fig. 2, the cocatalytic efficiency of a metal ion depends on its hardness: harder metal ions can form more stable 5-membered rings, which can more readily help to cleave the glycosidic bond in the key step of the hydrolysis. This mechanism explains why the hard metal salts (entries 10, 11, 13, 17, 18 and 26 in Table 2) considerably accelerate the hydrolysis, whereas the soft ones (entries 1–5 in Table 2) could not.

4. Conclusion

$SrCl_2$ was found to be the most efficient cocatalyst for the acidic hydrolysis of methyl glycosides among 26 metal salts screened as Lewis acid. The $SrCl_2$-cocatalyzed acidic hydrolysis of methyl glycosides was highlighted by short reaction times, less byproducts and high yields. Based on this work, the best conditions for acidic hydrolysis of methyl glycosides included heating the methyl glycosides in a mixed solvent consisting of 5 mol/L HCl/acetic acid (1/6, v/v) with 0.1 eq. of $SrCl_2$ as cocatalyst at 70 °C. This strategy solved the problems of the hydrolysis of methyl glycosides, particularly the formation of large quantities of byproducts and poor yields, where there are no acceptable methods currently available.

Acknowledgments

The authors are very grateful to the Natural Science Foundation of China (No. 21302141) and the Key Projects of Tianjin Science and Technology Support Plan (No. 10ZCKFSH01300) for financial support.

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