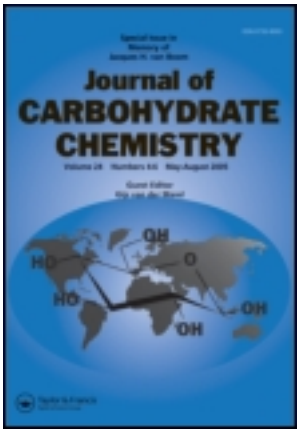

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Ultrasound-Assisted Selective Deprotection of Terminal Acetonides Catalyzed by Silica-Supported Boron Trifluoride

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Ultrasound-Assisted Selective Deprotection of Terminal Acetonides Catalyzed by Silica-Supported Boron Trifluoride

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An efficient and convenient method for the selective cleavage of terminal acetonides is described. Treatment of terminal acetonides in the presence of a wide range of functional groups with silica-supported boron trifluoride as a catalyst furnished the corresponding diols in 82–95% yield under ultrasound irradiation conditions. The acid-labile *p*-methoxybenzyl group as a protecting group remained intact under the conditions employed to the present deprotection condition.

Keywords Carbohydrate; Acetonide; Ultrasound; Silica-supported; Boron trifluoride

INTRODUCTION

Selective protection and deprotection of hydroxyl groups are the key to the success of oligosaccharide synthesis.[1] It is well known that the acetonide group is one of the most utilized moieties to protect both terminal and internal 1,2- and 1,3-diols in carbohydrate and nucleoside chemistry.[2] As a result, a variety of catalysts have been employed for the deprotection of terminal acetonides, including protonic acids such as HCl,[3a] HBr,[3b] HOAc,[3c] H_2SO_4,[3d] and TFA[3e] and Lewis acid–based reagents such as $(Zn(NO_3)_2.6H_2O$,[4a] $CeCl_3.7H_2O(COOH)_2$,[4b] VCl_3,[4c] $BiCl_3$,[4d] $La(NO_3)_3$,[4e] and $In(OTf)_3$.[4f] Nevertheless, many of these procedures suffer from disadvantages such as too strongly acidic conditions,[3d,3e] expensive metals used,[4c–e]

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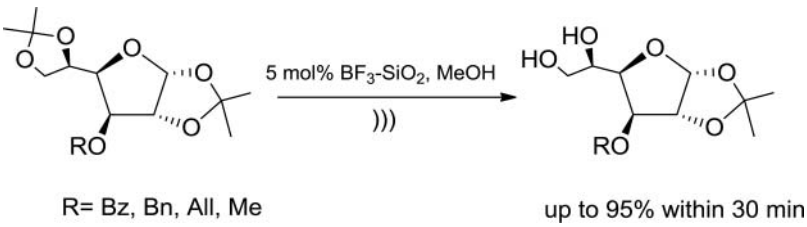
long reaction times,[4e] and high reaction temperatures.[4f] Additionally, the protonic acids or Lewis acid–based reagents are used in homogeneous solutions, making the removal of these catalysts a problem. Alternatively, supported reagents including $FeCl_3.6H_2O$ on silica,[5a] H_2SO_4 on silica,[5b] $HClO_4$ on silica,[5c] and $NaHSO_4$ on silica[5d] have been employed for this transformation. Though easily removed as they might be, they are endowed with some drawbacks, including lower yields,[5a] long reaction times,[5c] and incompatibility with some other protecting groups.[5d]

Boron trifluoride has been widely used as a Lewis acid catalyst in many organic reactions.[6a–d] The silica-supported boron trifluoride (BF_3-SiO_2) is a bench-top reagent, which is inexpensive, eco-friendly, and reusable. It is efficient to promote many acid-catalyzed organic reactions.[7] Ultrasound activation has been emerging as a powerful technique to enhance reaction rates of a variety of chemical transformations.[8] In particular, the beneficial effects of ultrasonic irradiation play an increasingly important role in chemical processes, especially in the cases where classical methods require drastic conditions or prolonged reaction times.[9]

Along this line, herein we disclose an efficient and facile method for the selective deprotection of terminal acetonides with BF_3-SiO_2 in methanol under ultrasound irradiation (Sch. 1). To the best of our knowledge, the ultrasound-assisted deprotection of terminal acetonides has not yet been reported in the literature.

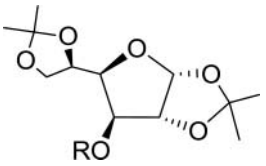
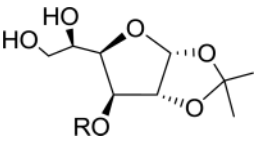
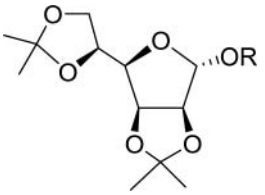
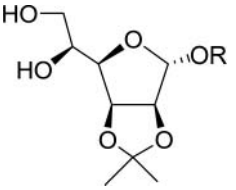


Scheme 1: Selective hydrolysis of the terminal *O*-isopropylidene with BF_3-SiO_2

RESULTS AND DISCUSSION

As a model reaction, we treated 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **1a** (entry 1, Table 1) with 5 mol% of BF_3-SiO_2 as a catalyst in the absence or presence of ultrasound irradiation at room temperature in methanol, respectively. In the case of absence of ultrasound irradiation, the reaction mixture was stirred for 3 h to give product **2a** in a moderate yield of 78%, while the application of ultrasound irradiation resulted in the dramatic decrease of reaction time (0.5 h), maintaining an excellent yield of 85%. It should be noted that only the product with terminal acetonide removed was detected under the above conditions. Encouraged by this result, we applied a set of carbohydrate

Table 1: Selective cleavage of terminal acetonides using BF_3-SiO_2[a]

Entry	Substrate	Product	Time (min) Stirring	Time (min))))[c]	Yield (%)[b] Stirring	Yield (%)[b])))
						
1	**1a** R = H	**2a** R = H[10a]	180	30	78	85
2	**1b** R = Bz	**2b** R = Bz[4d]	180	30	76	89
						
3	**1f** R = Bz	**2f** R = Bz[4a]	150	30	82	90
4	**1g** R = Bn	**2g** R = Bn[4e]	180	30	81	92

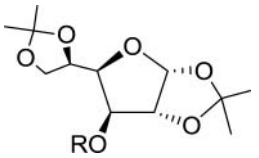
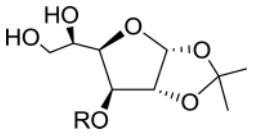
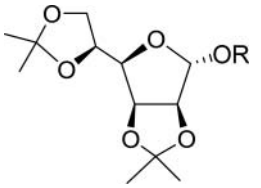
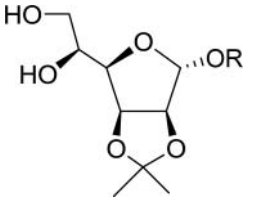
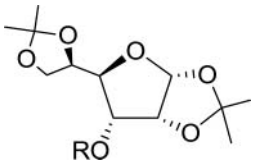
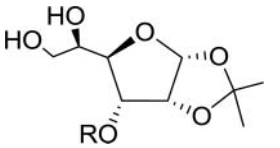
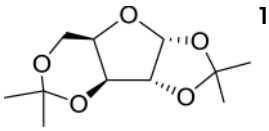
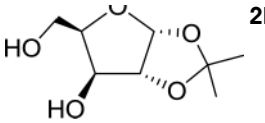
[a]The structures of the products were established by ^{1}H NMR data.
[b]Isolated yields.
[c]))) under ultrasound irradiation.

substrates to the condition to investigate the ultrasonic effect. The results are listed in Table 1. When substrates **1b**, **1f**, and **1g** were exposed to the ultrasound irradiation, yields of the corresponding products **2b**, **2f**, and **2g** increased from 76%, 82%, and 81% to 89%, 90%, and 92%, respectively, as compared to reaction without ultrasound irradiation. In addition, in all of the cases tested here, the reaction time was dramatically shortened.

Reactions under heating condition without ultrasound irradiation were also carried out for comparison. We treated compound **1a** and **1b** with 5 mol% BF_3-SiO_2 as catalyst in methanol at 50°C, and the reaction mixtures were stirred for 1.5 h to give corresponding products **2a** and **2b** in yields of 79% and 80%, respectively. Apparently, heating could shorten the reaction time to a certain extent, but the effect was not comparable to ultrasonication.

To explore the scope of the applicability of this deprotection methodology, substrates with terminal acetonides and a wide range of other functional groups were investigated under the above ultrasound irradiation condition (Table 2). The substrate 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1c**) furnished the corresponding diol **2c** in an isolated yield of 87% within 35 min (entry 3). A diacetonide derivative of D-glucose **1d** that contained an allyl ether linkage produced the corresponding diol product **2d**

Table 2: Selective cleavage of terminal acetonides using BF_3-SiO_2 under ultrasound irradiation[a]

Entry	Substrate	Product	Time (min)	Yield (%)[b]
				
1	**1a** R = H	**2a** R = H[10a]	30	85
2	**1b** R = Bz	**2b** R = Bz[4d]	30	89
3	**1c** R = Bn	**2c** R = Bn[4d]	35	87
4	**1d** R = All	**2d** R = All[10b]	35	92
5	**1e** R = Me	**2e** R = Me[10c]	30	95
				
6	**1f** R = Bz	**2f** R = Bz[4a]	30	90
7	**1g** R = Bn	**2g** R = Bn[4e]	30	92
8	**1h** R = All	**2h** R = All[11]	30	88
9	**1i** R = Me	**2i** R = Me[4d]	30	89
				
10	**1j** R = MOM	**2j** R = MOM	30	82
11	**1k** R = PMB	**2k** R = PMB	30	88
12	 **1l**	 **2l**[2a]	40	85

[a]The structures of the products were established by their ^{1}H NMR data.
[b]Isolated yields.

in an excellent yield of 92% within 35 min (entry 4), and 3-*O*-methyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1e**) afforded the corresponding diol **2e** in a yield of 95% (entry 5) within 30 min. Similarly, a series of D-mannose derivatives containing Bz, Bn, All, and Me groups also furnished the expected corresponding diols in good to excellent yields (entries 6–9). To our delight, the diacetonide derivative of D-allose possessing the acid-labile *p*-methoxybenzyl

(PMB) group (**1k**) underwent a clean deprotection reaction to produce the corresponding diol **2k** in a good yield, under which condition the PMB group was unaffected (entry 11). In the case of D-xylofuranose derivative, reaction of 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose (**1l**) under the established condition produced the corresponding diol (**2l**) in a good yield of 85% (entry 12). Apparently, all the experiments were performed in relatively short time (30–40 min) and in good yields.

In summary, we have utilized BF_3-SiO_2 as an excellent catalyst for the selective deprotection of terminal acetonides under ultrasound irradiation conditions. The use of ultrasound irradiation not only speeded up the reaction process but also improved the reaction yields. Furthermore, acid-sensitive groups were found to be stable under this reaction condition. In addition, the use of solid-supported Lewis acid offers substantial advantages with respect to simplifying the reaction and workup procedures. We expected this methodology to find applications in oligosaccharide synthesis.

EXPERIMENTAL

General Methods

^{1}H NMR spectra were recorded with a Bruker DPX400 spectrometer in $CDCl_3$ solutions. Internal references: TMS (δ 0.00 ppm for ^{1}H), $CDCl_3$ (δ 77.00 ppm for ^{13}C). Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 5% (v/v) H_2SO_4 in CH_3OH or by UV detection. Column chromatography was conducted by elution of a column of silica gel (200–300 mesh) with EtOAc/petroleum ether (bp. 60–90°C) as the eluent. Solutions were concentrated at a temperature <60°C under diminished pressure.

The ultrasound-assisted reactions were carried out in a KUDOS®. SK5200H Ultrasonic Bath Cleaner, with a frequency of 53 kHz. The ultrasonic cleaner had a power consumption of 200 W (305 × 250 × 285 mm) with a liquid-holding capacity of 10 L. The reactions were carried out in a round-bottomed flask of 25-mL capacity suspended at the center of the cleaning bath, 5 cm below the surface of the liquid. The reaction flask was located in the cleaner, where the surface of reactants is slightly lower than the level of the water. The reaction temperature was controlled by addition or removal of water from an ultrasonic bath.

Preparation of BF_3-SiO_2 Reagent System[12]

Five milliliters of methanol containing 0.6 g (4.2 mmol) of $BF_3.OEt_2$ and 0.4 g of unpreheated silica gel was stirred for 1 h at rt. The slurry was dried slowly on

a rotary evaporator at 40°C. The obtained solid was dried at ambient temperature for 2 h. The BF_3-SiO_2 reagent system could be stored in a dry container (the drying agent is dry silica particles) for at least 3 months.

General Procedure for the Deprotection of Terminal Acetonides Catalyzed by BF_3-SiO_2 Under Ultrasound Irradiation

To a solution of acetonides of sugar derivatives (1 mmol) in CH_3OH (10 mL), BF_3-SiO_2 (5 mmol%) was added and the heterogeneous mixture was agitated in an ultrasonic cleaner at rt for the required time. After complete conversion, the mixture was filtered and washed with CH_3OH (5 mL). The combined filtrate was concentrated under vacuum and the residue was purified by column chromatography to obtain the pure product.

The products were characterized by ^{1}H NMR, and the spectroscopic data were identical with the data reported in the literature. Spectral data for new compounds, which were not reported earlier, are presented below.

1, 2-*O*-Isopropylidene-3-*O*-methoxymethyl-α-D-allofuranose (2i)

Viscous liquid, $[\alpha]_D^{25}$ −49.6 (c 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ:* 5.77 (d, $J = 3.6$ Hz, 1H), 4.74 (d, $J = 4.0$ Hz, 1H), 4.70–4.65 (m, 2H), 4.24–4.13 (m, 3H), 4.06 (d, $J = 3.0$ Hz, 1H), 3.43 (s, 3H), 1.58 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 111.51, 104.67, 96.61, 82.89, 80.77, 79.37, 68.23, 63.82, 55.67, 26.25, 25.77; HRMS (ESI) calcd for $C_{11}H_{20}NaO_7$ $(M + Na)^+$ 287.1101, found 287.1102.

1, 2-*O*-Isopropylidene-3-*O*-*p*-methoxybenzyl-α-D-allofuranose (2j)

Viscous liquid, $[\alpha]_D^{25}$ −51.51 (c 1.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.30 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 5.75 (d, $J = 3.6$ Hz, 1H), 4.72 (d, $J = 11.2$ Hz, 1H), 4.60 (t, $J = 3.6$ Hz, 1H), 4.50 (d, $J = 11.2$ Hz, 1H), 4.09 (dd, $J = 9.2$, 3.6 Hz, 1H), 3.99 (m, 1H), 3.91 (dd, $J = 8.8$, 4.4 Hz, 1H), 3.80 (s, 3H), 3.65–3.69 (m, 2H), 2.70 (br s, 1H), 2.69 (br s, 1H), 1.59 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.09, 129.18, 128.79, 113.62, 111.33, 104.68, 81.71, 81.07, 79.39, 71.36, 68.78, 63.84, 54.85, 26.26, 25.76; HRMS (ESI) calcd for $C_{17}H_{24}NaO_7$ $(M + Na)^+$ 363.1414, found 363.1411.

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