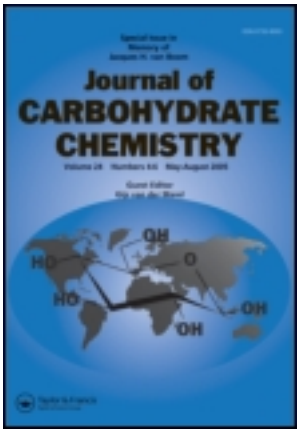

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Synthesis of Thioglycosides in Room Temperature Ionic Liquid

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Synthesis of Thioglycosides in Room Temperature Ionic Liquid

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An eco-friendly reaction for the preparation of thioglycosides has been developed using an ionic liquid as the solvent. Thioglycosides were obtained in excellent yields on treatment of per-*O*-acetylated sugar derivatives with thiols in the presence of boron trifluoride diethyl etherate in [Bmim][BF_4] as solvent at 20°C. *Supplemental materials are available for this article. Go to the publisher's online edition of* Journal of Carbohydrate Chemistry *to view the free supplemental file.*

Keywords Thioglycoside; Ionic liquid; Eco-friendly; Boron trifluoride diethyl etherate; [Bmim][BF_4]

INTRODUCTION

Thioglycosides are widely used glycosyl donors in the synthesis of oligosaccharides.[1–4] They have been used as intermediates for the preparation of glycosyl fluorides,[5] sulfoxides, and sulfone derivatives, which are also considered as useful glycosyl donors in glycoside synthesis.[6–9] Because of their close similarity with their *O*-glycoside counterparts and stability against enzymatic cleavage, a number of reports appeared using thioglycosides in several biochemical and structural studies.[10–14] Because of the great stability of thioglycosides under a wide range of reaction conditions for protecting group manipulations, they can serve as effective glycosyl donors as well as glycosyl acceptors. This orthogonal property of thioglycosides has been successfully exploited in the synthesis of complex oligosaccharides.[15,16] A number of reports have appeared in the literature for the preparation of thioglycosides, essentially following a general concept of reaction of acetylated sugar derivatives with thiols or thiol

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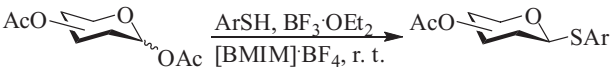
derivatives in the presence of a Lewis acid.[17–24] However, these methods suffer from a number of drawbacks such as use of excess chlorinated organic solvents, malodorous thiols, control of temperature, and anomerization of products. A few odorless reaction protocols have also appeared in the literature for the preparation of thioglycosides including either treatment of glycosyl thiouronium salts[25,26] with alkyl halides or reductive cleavage of disulfides followed by treatment with glycosyl halides.[27] Although these methods are comparatively odorless, they require either pregeneration of *S*-glycosyl isothiouronium salts from relatively unstable glycosyl halides or reductive cleavage of disulfides before reacting with glycosyl halides. Despite their usefulness, the abovementioned methods have a major shortcoming because of the use of a large quantity of chlorinated organic solvents. In an endeavor to develop a clean, organic, solvent-free synthesis of thioglycosides, we sought to evaluate the use of eco-friendly room temperature ionic liquids (RTIL) in the preparation of thioglycosides. In the recent past, ionic liquids have gained considerable attention from synthetic organic chemists because of their potential to act as solvents in several organic transformations under green reaction conditions.[28,29] Ionic liquids have been used in various synthetic methodologies for the transformation of carbohydrates such as acetylation,[30] benzylidenation,[31] orthoesterification,[32] Ferrier rearrangement of glycols,[33] Fischer glycosylation,[34] and activation of thioglycosides[35,36] and glycosyl trichloroacetimidate derivatives[37,38] in glycosylations. There is no report for the preparation of thioglycoside derivatives using ionic liquids. We report herein an efficient preparation of thioglycoside derivatives using 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), a frequently available rt ionic liquid, avoiding chlorinated organic solvents (Sch. 1).



Scheme 1: Preparation of thioglycoside by treatment of sugar acetate with thiol in the presence of BF_3·OEt_2 in ionic liquid.

RESULTS AND DISCUSSION

Initially, β-D-glucose penta-acetate (**1**) was allowed to react with a varied quantity of thiophenol (1.0 to 2.0 equiv.) in the presence of borontrifluoride diethyletherate (BF_3·OEt_2; 1.0 to 2.0 equiv.) in 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) (0.5 mL to 2.0 mL per mmol of substrate) at 0°C to rt. After a series of experiments, it was observed that the use of 1.2 equiv. thiophenol in the presence of 1.2 equiv. of BF_3·OEt_2 in 1.0 mL [Bmim][BF_4] per mmol of substrate could furnish 91% yield of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**9**) in 40 min at 20°C. Following a similar reaction

condition a series of per-*O*-acetylated thioglycoside derivatives were prepared from different acetylated sugar derivatives in excellent yields (80% to 92%), which are presented in Table 1. The products were obtained by extraction with diethyl ether and aqueous workup. Exclusive 1,2-*trans* thioglycoside derivatives were obtained in most of the cases, except minor quantities (~5% to 10%) of 1,2-*cis* products in some cases. Presumably the 1,2-*cis* products were formed due to the anomerization of the kinetically controlled 1,2-*trans* products under acidic reaction conditions. A scale-up reaction using 10 mmol of compound **1** and *p*-thiocresol under similar reaction conditions furnished 84% yield of compound **10**. All known products gave acceptable spectral data matched with the cited references. A number of imidazolium ionic liquids (e.g., [Bmim][PF_6], [Bmim][OTf]) have also been examined as reaction solvents. The best results were obtained using [Bmim][BF_4] in terms of solubility of the substrates and yield of the products obtained (Table 2). Presumably, the structure of ionic liquid [Bmim][BF_4] influences the reaction and BF_4^- could be a better counteranion to facilitate the thioglycosylation using $BF_3{\cdot}OEt_2$.

In order to study the recycling property of the ionic liquid, after completion of the reaction it was extracted with diethyl ether. The remaining ionic liquid was successively washed with toluene and water. The solvents were removed under reduced pressure to give the ionic liquid, which was dried at 70°C under reduced pressure. The recovered ionic liquid was reused for thioglycosylation at least four times without significant loss of efficiency, providing a similar yield of thioglycoside derivatives (Table 1, entry 1).

In summary, a novel, eco-friendly, reasonably fast, high-yielding methodology has been developed for the preparation of thioglycosides using [Bmim][BF_4] ionic liquid. [Bmim][BF_4] can be recycled and reused several times without any loss of efficiency.

EXPERIMENTAL

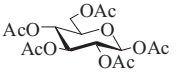
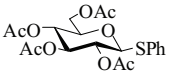
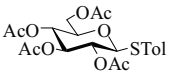
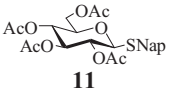
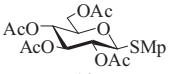
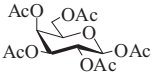
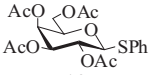
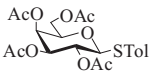
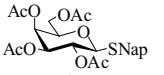
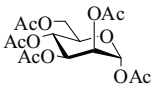
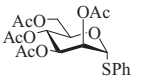
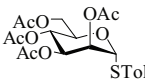
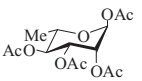
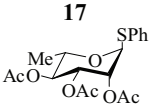
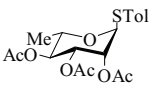
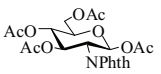
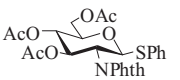
General Methods

All reactions were monitored by thin layer chromatography over silica gel–coated TLC plates. The spots on TLC were visualized by warming ceric sulphate (2% $Ce(SO_4)_2$ in 2N H_2SO_4) sprayed plates in hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR were recorded on Brucker Avance DRX 500 MHz using TMS as internal reference. Chemical shift value is expressed in δ ppm.

Typical Experimental Condition

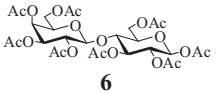
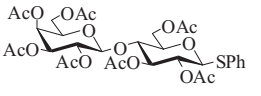
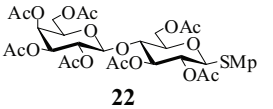
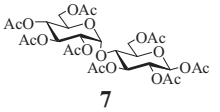
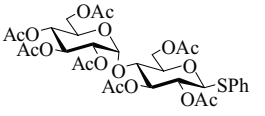
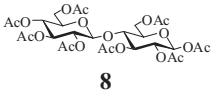
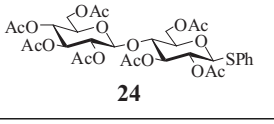
To a mixture of penta-*O*-acetyl-β-D-glucopyranose (**1**; 390 mg; 1.0 mmol) and thiophenol (125 μL, 1.2 mmol) in [Bmim][BF_4] (1.0 mL) was added

Table 1: $BF_3{\cdot}OEt_2$-catalyzed synthesis of thiglycosides in ionic liquid (Bmim)(BF_4) at 20°C

Sl. No.	Substrate	Thiol	Product	Time (min)	Yield (%)	Ref.
1	 **1**	Thiophenol	 **9**	40	91 90[a] 90[b] 87[c]	(39)
2		p-Thiocresol	 **10**	40	92 84[d]	(23)
3		2-Thionapthol	 **11**	60	88[e]	(40)
4		4-Methoxy thiophenol	 **12**	40	90	—
5	 **2**	Thiophenol	 **13**	40	92	(41)
6		p-Thiocresol	 **14**	40	93[f]	(23)
7		2-Thionapthol	 **15**	60	82[g]	(40)
8	 **3**	Thiophenol	 **16**	40	87	(42)
9		p-Thiocresol	 **17**	40	85	(23)
10	 **4**	Thiophenol	 **18**	30	90	(43)
11		p-Thiocresol	 **19**	30	88	(23)
12	 **5**	Thiophenol	 **20**	45	86	(44)

(Continued on next page)

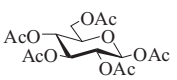
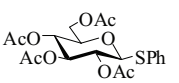
Table 1: $BF_3{\cdot}OEt_2$-catalyzed synthesis of thiglycosides in ionic liquid (Bmim)(BF_4) at 20°C *(Continued)*

Sl. No.	Substrate	Thiol	Product	Time (min)	Yield (%)	Ref.
13	 **6**	Thiophenol	 **21**	45	90	(45)
14		4-Methoxy thiophenol	 **22**	60	82	—
15	 **7**	Thiophenol	 **23**	60	80	(45)
16	 **8**	Thiophenol	 **24**	60	85	(45)

[a] Yield in first recycled IL.
[b] Yield in second recycled IL.
[c] In third recycled IL.
[d] Reaction carried out with 4.0 g (10.25 mmol) of compound **1**.
[e] Together with ~8% α-product.
[f] Together with ~5% α-product.
[g] Together with ~10% α-product.
Ph, Phenyl; Tol, 4-methylphenyl; Nap, 2-Napthyl; Mp, 4-methoxyphenyl.

$BF_3{\cdot}OEt_2$ (150 μL, 1.2 mmol) and the reaction mixture was allowed to stir at 20°C for 40 min. After completion, the reaction mixture was extracted with diethyl ether. The organic layer was successively washed with satd. $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated under reduced pressure to give crude product, which was purified by column chromatography using hexane-EtOAc (5:1) as eluent to furnish pure phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**9**; 400 mg; 91%). To the remaining ionic liquid was added

Table 2: Comparison of the yields of the thioglycosylation of D-glucose penta-*O*-acetate (**1**) using thiophenol and $BF_3{\cdot}OEt_2$ in different ionic liquids (IL)

Sl. No.	Substrate	Product	Ionic liquid	Yield (%)
1	 **1**	 **9**	(Bmim)(BF_4)	91
2			(BMIM)(PF_6)	72
3			(BMIM) (OTf)	63
4			(BMIM) (Cl)	30

water and it was washed with toluene. The water layer was concentrated under reduced pressure to give ionic liquid, which was dried at 70°C under reduced pressure before its reuse.

Spectral Data of New Compounds

*4-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (12)*

White solid; m.p. 164–165°C; $[\alpha]_D^{25}$ −22 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44 (d, $J = 9.2$ Hz, 2 H, Ar-H), 6.84 (d, $J = 9.2$ Hz, 2 H, Ar-H), 5.19 (t, $J = 9.2$ Hz each, 1 H, H-3), 4.99 (t, $J = 9.8$ Hz each, 1 H, H-2), 4.89 (t, $J = 9.2$ Hz each, 1 H, H-4), 4.54 (d, $J = 9.8$ Hz, 1 H, H-1), 4.22–4.15 (m, 2 H, H-6), 3.81 (s, 3 H, OCH_3), 3.69–3.65 (m, 1 H, H-5), 2.10, 2.07, 2.01, 1.98 (4 s, 12 H, 4 COCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 170.2, 169.4, 169.2 (4 *C*OCH$_3$), 160.4-114.4 (Ar-C), 85.6 (C-1), 75.7, 74.0, 69.8, 68.2, 62.0 (C-6), 55.3 (O*C*H$_3$), 20.8, 20.7 (2 C), 20.6 (4 CO*C*H$_3$); ESI-MS: $m/z = 493.1$ $[M+Na]^+$; Anal. Calcd. for $C_{21}H_{26}O_{10}S$ (470.12): C, 53.61; H, 5.57%; found: C, 53.40; H, 5.83%.

*4-Methoxyphenyl (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (22)*

White solid; m.p. 167–168°C; $[\alpha]_D^{25}$ −21 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (d, $J = 9.2$ Hz, 2 H, Ar-H), 6.84 (d, $J = 9.2$ Hz, 2 H, Ar-H), 5.33 (br s, 1 H, H-4_B), 5.18 (t, $J = 9.2$ Hz each, 1 H, H-3_A), 5.08 (dd, $J = 7.9$, 7.9 Hz, 1 H, H-2_A), 4.94 (dd, $J = 10.3$, 3.4 Hz, 1 H, H-3_B), 4.80 (t, $J = 9.7$ Hz each, 1 H, H-2_B), 4.55–4.52 (dd, $J = 11.9$, 1.7 Hz, 1 H, H-6_{aA}), 4.50 (d, $J = 10.0$ Hz, 1 H, H-1_B), 4.44 (d, $J = 7.9$ Hz, 1 H, H-1_A), 4.13–4.0 (m, 3 H, H-6_{abB} and H-6_{bA}), 3.86–3.82 (m, 1 H, H-5_A), 3.80 (s, 3 H, OCH_3), 3.70 (t, $J = 9.8$ Hz each, 1 H, H-4_A), 3.59–3.56 (m, 1 H, H-5_B), 2.14, 2.10, 2.03, 2.02, 2.00, 1.95 (6 s, 21 H, 7 COCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.3, 170.2, 170.1, 170.0, 169.7, 169.5, 169.0 (7 *C*OCH$_3$), 160.3–114.3 (Ar-C), 100.0 (C-1′), 85.4 (C-1), 76.6, 76.0, 73.9, 70.9, 70.6, 70.2, 69.0, 66.6, 61.9 (C-6), 60.7 (C-6′), 55.3 (O*C*H$_3$), 20.9, 20.8, 20.7, 20.6 (3 C), 20.5 (7 CO*C*H$_3$); ESI-MS: $m/z = 781.2$ $[M+Na]^+$; Anal. Calcd. for $C_{33}H_{42}O_{18}S$ (758.21): C, 52.24; H, 5.58%; found: C, 52.00; H, 5.85%.

ACKNOWLEDGEMENT

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