

Bi(OTf)₃ and SiO₂-Bi(OTf)₃ as Effective Catalysts for the Ferrier Rearrangement[#]

J. Lokesh Babu ¹, Anakshi Khare ² and Yashwant D. Vankar ^{1,*}

¹ Department of Chemistry, Indian Institute of Technology Kanpur 208 016, India. Fax: (+91)-512-259 7492.

² Department of Chemistry, University of Lucknow, Lucknow 226 006, India.

* Author to whom correspondence should be addressed. E mail: vankar@iitk.ac.in

[#] This paper is dedicated to Prof. K. K. Balsubramanian on his 65th birthday.

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Abstract: Bi(OTf)₃ and SiO₂-Bi(OTf)₃ are found to effectively catalyze the Ferrier rearrangement of tri-O-acetyl glycols with different alcohols providing an effective route to 2,3-unsaturated *O*-glycosides with good anomeric selectivity and good to excellent yields after short reaction times.

Keywords: Glycols, pseudoglycols, glycosidation, bismuth triflate, Ferrier rearrangement.

Introduction

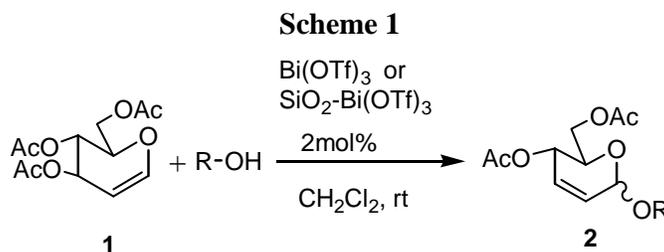
The Lewis acid catalyzed allylic rearrangement of glycols in the presence of alcohols is known as the Ferrier rearrangement [1]. This rearrangement leads to the formation of alkyl and aryl 2,3-unsaturated-*O*-glycosides, which are versatile chiral intermediates in the synthesis of several biologically active natural products [2]. 2,3-Unsaturated-*O*-glycosides are also important building blocks in the synthesis of some antibiotics [3]. The Ferrier rearrangement involves the intermediacy of an allylic oxycarbenium ion to which the nucleophile adds preferentially in a quasi-axial orientation. The Lewis acid catalysts used for this rearrangement include BF₃·OEt₂ [4], SnCl₄ [5] and FeCl₃ [6]. Other reagents such as DDQ [7], NIS [8], I₂ [9], acidic Montmorillonite K-10 [10], BiCl₃ [11] and

InCl_3 [12] are also known to bring about the Ferrier rearrangement under different conditions. In recent years $\text{Sc}(\text{OTf})_3$ [13] and $\text{Yb}(\text{OTf})_3$ [14] have also been employed for the Ferrier rearrangement. However, many of these procedures have limitations in terms of yields, stereoselectivities, reaction temperatures, reaction times and amounts of reagent or catalyst used. For example, 1.6 equivalents of NIS [8], or varied amounts of $\text{BF}_3 \cdot \text{OEt}_2$ [4] are needed to bring about the transformation. Reagents such as $\text{Sc}(\text{OTf})_3$ and $\text{Yb}(\text{OTf})_3$ are relatively expensive and while using $\text{Yb}(\text{OTf})_3$ for this transformation, the reaction time is somewhat longer in some cases (see Table 2). Therefore, there is a need for the introduction of convenient and inexpensive reagents which are cheaper, require shorter reaction times and offer good anomeric selectivity.

To this end bismuth(III) trifluoromethane sulfonate (bismuth triflate) [$\text{Bi}(\text{OTf})_3$], has drawn our attention for use in the Ferrier rearrangement as it is cheap, easy to prepare [15], and has low toxicity. Bismuth triflate has been used as a catalyst for the Friedel-Crafts acylation [16], sulfonylation of arenes [17], the Diels-Alder reaction [18], aza Diels-Alder reaction [19], acylation of alcohols [20], epoxide rearrangements [21] and acylal synthesis [22].

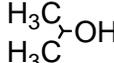
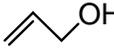
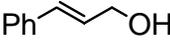
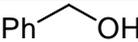
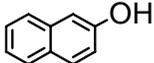
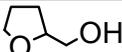
Results and Discussion

Herein, we wish to report that $\text{Bi}(\text{OTf})_3$ acts as a mild and highly efficient reagent for the *O*-glycosylation of 3,4,6-tri-*O*-acetylglucal (**1**) with diverse alcohols (Scheme 1). The glycosylation of tri-*O*-acetyl glucal with primary, secondary, benzyl, allyl and propargyl alcohols proceeded smoothly at ambient temperature to afford, after short reaction times, the corresponding alkyl 2,3-unsaturated glycosides **2** in good to high yields, with the α -anomer being the major or the exclusive product. Our results are summarized in Table 1. As shown there, these glycosylation reactions proceed smoothly in the presence of 2 mol % of $\text{Bi}(\text{OTf})_3$ or 2 mol% of the catalyst supported on 250 mg of SiO_2 in dichloromethane per 100 mg of the 3,4,6-tri-*O*-acetylglucal substrate. In all the given examples, except for entry 12 (β -naphthol), the corresponding *O*-glycosylation products are obtained. In the case of entry 12 the corresponding 1-*C*-glucoside was obtained, presumably via rearrangement of the corresponding *O*-glucoside. Formation of the *C*-glucoside was confirmed by its acetylation followed by the characterization of the corresponding acetylated product by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, IR and mass spectral data (cf. Experimental section).



Further, we have also found that bismuth triflate supported on silica gel also acts as an efficient reagent for the above transformation. The use of SiO_2 -supported $\text{Bi}(\text{OTf})_3$ reagent had in some cases interesting effects in terms of yield (entries 9,10,14), reaction time (entries 1, 3, 13) and selectivity (entries 1, 2, 5), as can be seen in Table 1. Therefore it appears that increasing the surface of the catalyst is advantageous in certain cases, although it reduces the reactivity. It is therefore clear that either of the reagents could be more useful, depending on the glycosyl acceptor.

Table 1. Bi(OTf)₃ catalyzed glycosylation of alcohols.

S. No.	Alcohol	Bi(OTf) ₃			Bi(OTf) ₃ – SiO ₂		
		Reaction time	Yield (%) ^a	Anomeric ratio(a:b) ^b	Reaction time	Yield (%) ^a	Anomeric ratio(a:b) ^b
1.	CH ₃ CH ₂ OH	1 h	78	5.5 : 1	40 min	72	12 : 1
2.	CH ₃ (CH ₂) ₂ OH	45 min	72	6 : 1	1 h	70	10 : 1
3.	CH ₃ OH	6 h	56	6.6 : 1	75 min	81	6.9 : 1
4.		20 min	70	5.5 : 1	45 min	60	5.3 : 1
5.	CH ₃ (CH ₂) ₇ OH	50 min	84	4.5 : 1	1 h	83	8.9 : 1
6.		3 min	75	α	2 h	51	α
7.		5 min	73	α	2.5 h	76	7.8 : 1
8.		30 min	82	α	2 h	80	3 : 1
9.		25 min	53	6 : 1	40 min	81	8.7 : 1
10.		3 min	69	4 : 1	15 min	90	2.2 : 1
11.	Cholesterol	2 h	70	α	3 h	74	15 : 1 ^c
12.		10 min	66	6 : 1	20 min	58	3.2 : 1 ^d
13.		12 min	73	16 : 1	5 min	61	12 : 1
14.		5 min	79	6 : 1	20 min	83	6 : 1

(a) Isolated yields

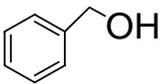
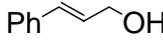
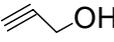
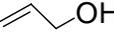
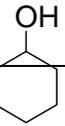
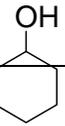
(b) Anomeric ratio is determined by ¹H-NMR (400MHz) spectroscopy.

(c) 4 mol % of the catalyst was used and reaction warmed to 40°C.

(d) Only C-Ferrier product is observed.

A comparison of the literature methods with the new Bi(OTf)₃ and Bi(OTf)₃-SiO₂ reagents is presented in Table 2. Although BiCl₃ is known [11] to bring about the Ferrier rearrangement (cf. entries 1, 3, 4 and 7, Table 2), it is clear from the data that with alcohols such as benzyl alcohol (entry 1), propargyl alcohol (entry 3), and allyl alcohol (entry 4) the time required using bismuth chloride is between 1 to 1.5 h, in comparison to 3 min required using Bi(OTf)₃.

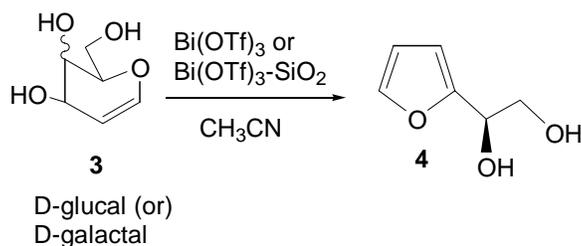
Table 2. Comparison of results of Bi(OTf)₃ with other catalysts

S.No.	Alcohol	Catalyst	Time	Yield (%)	(α : β) ratio	Amount of catalyst used
1.		CAN	3 h	90	7 : 1	10 mol %
		Sc(OTf) ₃	3.5 h	85	5 : 1	5 mol %
		Yb(OTf) ₃	3 h	94	9 : 1	10 mol %
		BiCl ₃	1 h	94	10 : 1	5 mol %
		InCl ₃	10 min	86	6.3 : 1	20 mol %
		Bi(OTf) ₃ -SiO ₂	15 min	90	2.2 : 1	2 mol %
		Bi(OTf) ₃	3 min	69	4 : 1	2 mol %
2.		CAN	2.5 h	89	9 : 1	10 mol %
		Sc(OTf) ₃	2.5 h	92	9 : 1	5 mol %
		Bi(OTf) ₃ -SiO ₂	40 min	81	8.7 : 1	2 mol %
		Bi(OTf) ₃	25 min	53	6 : 1	2 mol %
3.		CAN	6 h	80	4 : 1	10 mol %
		Sc(OTf) ₃	1.5 h	93	10 : 1	5 mol %
		Yb(OTf) ₃	4 h	91	10 : 1	10 mol %
		BiCl ₃	1.5 h	95	10 : 1	5 mol %
		Bi(OTf) ₃ -SiO ₂	2.5 h	76	7.8 : 1	2 mol %
		Bi(OTf) ₃	5 min	73	α	2 mol %
4.	 	CAN	3 h	90	4 : 1	10 mol %
		Sc(OTf) ₃	1.5 h	95	7 : 1	5 mol %
		BiCl ₃	1.5 h	95	11 : 1	5 mol %
		Bi(OTf) ₃ -SiO ₂	2 h	51	α	2 mol %
		Bi(OTf) ₃	3 min	75	α	2 mol %
		I ₂	1 h	88	7 : 1	20 mol %
5.		CAN	4.5 h	80	14 : 1	10 mol %
		Sc(OTf) ₃	3 h	83	7 : 1	5 mol %
		Yb(OTf) ₃	18 h	89	11 : 1	10 mol %
		InCl ₃	30 min	90	9 : 1	20 mol %
		Bi(OTf) ₃	30 min	82	α	2 mol %
		Bi(OTf) ₃ -SiO ₂	2 h	80	3 : 1	2 mol %
6.		CAN	4 h	87	7 : 1	10 mol %
		Sc(OTf) ₃	2 h	92	9 : 1	5 mol %
		Bi(OTf) ₃	5 min	79	6 : 1	2 mol %
		Bi(OTf) ₃ -SiO ₂	20 min	83	6 : 1	2 mol %
7.	Cholesterol	CAN	5 h	78	10 : 1	10 mol %
		BiCl ₃	2 h	90	4 : 1	5 mol %
		Bi(OTf) ₃	2 h	70	α	2 mol %
		Bi(OTf) ₃ -SiO ₂	3 h	74	15:1	2 mol %

Likewise, with allyl alcohol, propargyl alcohol and cholesterol (entry 7) the Ferrier product is a mixture of α and β anomers using bismuth chloride whereas with $\text{Bi}(\text{OTf})_3$ only the α anomer is obtained. In general, the amount of the BiCl_3 used is 5 mol%, whereas $\text{Bi}(\text{OTf})_3$ is used in only 2 mol% indicating that it is more reactive than BiCl_3 . Thus, overall it appears that $\text{Bi}(\text{OTf})_3$ has distinct advantages over BiCl_3 in terms of reaction time, selectivity, and amount of the catalyst required.

Furanoid skeletons (Scheme 2) are important components [23] of many biologically important natural products. Certain monosaccharides under acidic conditions lead to furans [24]. An optically active furandiols such as 2-(D-glycero-1,2-dihydroxyethyl)furan (**4**) is a potential chiral building block in organic synthesis [25]. The transformation of D-glucal **3** to furandiols **4** with the HgSO_4 -dioxane system was first reported by Gonzalez *et al.* [26]. Following this report, Hayashi *et al.* [27] screened several catalysts such as $\text{Pd}(\text{OAc})_2$, $\text{RuCl}_2(\text{PPh})_3$, $\text{Sm}(\text{OTf})_3$ and $\text{Yb}(\text{OTf})_3$ for the transformation of **3** into **4**, reporting yields ranging from 44% to 70% and requiring 30-165 minutes at 80-100°C, but some of these reagents are expensive and HgSO_4 is toxic. Some improved procedures for this transformation can be found in the literature. Recently, Balasubramanian *et al.* [28] used $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ for this purpose. The reaction requires 10 mol % of the catalyst and is completed in 2.5 h to give **4** in 82% yield. More recently, in our laboratory [29], HClO_4 - SiO_2 has been found to be an efficient acidic catalyst for the formation of **4** in 89% yield. It therefore seemed logical to focus our attention on the use of the present reagent system for the formation of **4**. Thus, use of 1 mol% of $\text{Bi}(\text{OTf})_3$ transformed D-glucal into **4** in after 1 h, albeit in only 59% yield. Increasing the amount of the catalyst from 1 mol% to 3 mol% reduced the reaction time to 15 minutes, but the yield also dropped to 47%. Reaction of galactal, on the other hand, required 2 mol% of $\text{Bi}(\text{OTf})_3$ and it took 5 minutes for the reaction to complete, resulting in a 47% yield of the diol **4**.

Scheme 2



Conclusions

We have developed a highly stereoselective, $\text{Bi}(\text{OTf})_3$ and $\text{SiO}_2\text{-Bi}(\text{OTf})_3$ catalyzed Ferrier glycosylation to produce 2,3-unsaturated glycosides. Compared to other methods, our method appears to have advantages such as easy preparation of the inexpensive catalyst, shorter reaction times, good yields, high anomeric selectivity, mild reaction conditions and low catalyst loadings. We believe that it should find use in organic synthesis.

Acknowledgements

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Experimental:

General

All the alcohols used for the reactions are commercially available and were purchased from different chemical companies. All liquid alcohols were freshly distilled before use and solid alcohols were recrystallized. CH₃CN was dried over P₂O₅ followed by over CaH₂. After distillation it was stored over 4Å molecular sieves and used directly for the reactions. Dichloromethane was dried over anhydrous CaCl₂ and freshly distilled over CaH₂ prior to use. All reactions were carried out under an inert nitrogen atmosphere. All products were purified by silica gel column chromatography (100-200 mesh) using pet. ether and ethyl acetate as the eluents. Proton NMR spectra were recorded on a Jeol 400 MHz NMR spectrometer using CDCl₃ as the solvent. The yields reported are after purification. All compounds are known and the structures were confirmed by ¹H-NMR and ¹³C-NMR spectra and comparison of physical properties with the available literature data.

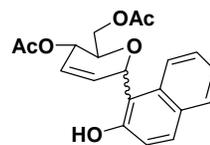
Preparation of the silica gel supported catalyst

Bismuth triflate (40 mg) was dissolved in dry CH₃CN (4 mL). To this solution was added activated silica gel (2g, 100-200 mesh) and a slurry was prepared by evaporating the solvent under vacuum. The slurry is kept under a nitrogen atmosphere and 250 mg of this reagent, which contains 2 mol % (5mg) of bismuth triflate, is used for each reaction.

General synthetic procedure

To a stirred mixture of tri-*O*-acetyl D-glucal (100 mg, 0.3676 mmol) and alcohol (1.1 eq) in dichloromethane (3 mL) under nitrogen was added 2 mol% of Bi(OTf)₃ (5 mg) at ambient temperature and the reaction was monitored by TLC. After the reaction was over, the reaction mixture was quenched with 20% aqueous NaHCO₃ solution and the crude product was extracted with dichloromethane (3 x 10 mL). The combined organic layers were washed with water, brine, and finally dried over anhydrous Na₂SO₄. Pure compound was obtained by column chromatography on SiO₂ (100-200 mesh).

Spectral data for the 1-*C*-glucoside corresponding to entry 12:



¹H-NMR (400 MHz, CDCl₃) (α -anomer) δ : 2.13 (s, 3H), 2.15 (s, 3H), 4.08-4.11 (dt, $J = 2.92, 5.84, 9.28$ Hz, 1H), 4.32-4.39 (m, 2H), 5.65 (dd, $J = 1.96, 9.28$ Hz, 1H), 5.87-5.90 (m, 1H), 5.97-6.00 (dd, 1H, $J = 4.4, 11.84$ Hz), 6.31 (brs, 1H), 7.09-7.79 (m, 6H), 8.53 (s, 1H). (β -anomer) δ : 8.34 (s, 1H), 6.11(brs, 1H); ¹³C-NMR (100 MHz, CDCl₃) (α -anomer) δ : 20.7, 20.9, 62.4, 64.2, 75.3, 75.3, 119.9, 120.6, 112.6-154.0 (10 aromatic carbons), 170.1, 170.8; IR(CH₂Cl₂) ν : 3362, 1742, 1622 1264, 1230 cm⁻¹; MSES⁺: 379 [M + Na]⁺, 295 [(M+2)-86+Na]⁺, 237 [M-143+Na]⁺. Acetate of 1-*C*-glucoside: ¹H-NMR (400 MHz, CDCl₃) (α -anomer) δ : 2.06 (s, 3H), 2.14 (s, 3H), 2.38 (s, 3H), 4.06-4.12 (m, 1H),

4.21-4.34 (m, 2H), 5.67-5.69 (m, 1H), 5.89-6.02 (m, 3H); ^{13}C -NMR (100 MHz, CDCl_3) (α -anomer) δ : 20.8, 21.0, 21.1, 63.5, 65.2, 71.6, 75.4, 121.4-146.7 (10 aromatic and 2 olefinic carbons), 169.6, 170.4, 171.0. IR (CH_2Cl_2) ν : 3055, 1740, 1232, 739 cm^{-1} . MSES $^+$: 819 $[\text{2M}+\text{Na}]^+$, 421 $[\text{M}+\text{Na}]^+$.

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