Bi(OTf)$_3$ and SiO$_2$-Bi(OTf)$_3$ as Effective Catalysts for the Ferrier Rearrangement\#  

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

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Abstract: Bi(OTf)$_3$ and SiO$_2$-Bi(OTf)$_3$ are found to effectively catalyze the Ferrier rearrangement of tri-O-acetyl glycals with different alcohols providing an effective route to 2,3-unsaturated \textit{O}-glycosides with good anomeric selectivity and good to excellent yields after short reaction times.  

Keywords: Glycals, pseudoglycals, glycosidation, bismuth triflate, Ferrier rearrangement.  

Introduction  

The Lewis acid catalyzed allylic rearrangement of glycals 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-\textit{O}-glycosides, which are versatile chiral intermediates in the synthesis of several biologically active natural products [2]. 2,3- Unsaturated-\textit{O}-glycosides are also important building blocks in the synthesis of some antibiotics [3]. The Ferrier rearrangement involves the intermediacy of an allylic oxy-carbenium ion to which the nucleophile adds preferentially in a quasi-axial orientation. The Lewis acid catalysts used for this rearrangement include BF$_3$·OEt$_2$ [4], SnCl$_4$ [5] and FeCl$_3$ [6]. Other reagents such as DDQ [7], NIS [8], I$_2$ [9], acidic Montmorillonite K-10 [10], BiCl$_3$ [11] and
InCl₃ [12] are also known to bring about the Ferrier rearrangement under different conditions. In recent years Sc(OTf)₃ [13] and Yb(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 BF₃·OEt₂ [4] are needed to bring about the transformation. Reagents such as Sc(OTf)₃ and Yb(OTf)₃ are relatively expensive and while using Yb(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) [Bi(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], sulfenylation 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 Bi(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 Bi(OTf)₃ or 2 mol% of the catalyst supported on 250 mg of SiO₂ 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 ¹H-NMR, ¹³C-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 SiO₂-supported Bi(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    | Yield (%)$^a$ | Anomeric ratio(a:b)$^b$ | Reaction    | 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.    | H$_3$C-CHOH- | 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.    | OH             | 3 min       | 75          | α                      | 2 h         | 51           | α                    |
| 7.    | OH             | 5 min       | 73          | α                      | 2.5 h       | 76           | 7.8 : 1               |
| 8.    | OH             | 30 min      | 82          | α                      | 2 h         | 80           | 3 : 1                 |
| 9.    | Ph-CHOH        | 25 min      | 53          | 6 : 1                  | 40 min      | 81           | 8.7 : 1               |
| 10.   | Ph-OH          | 3 min       | 69          | 4 : 1                  | 15 min      | 90           | 2.2 : 1               |
| 11.   | Cholesterol    | 2 h         | 70          | α                      | 3 h         | 74           | 15 : 1$^c$            |
| 12.   | OH             | 10 min      | 66          | 6 : 1                  | 20 min      | 58           | 3.2 : 1$^d$           |
| 13.   | OH             | 12 min      | 73          | 16 : 1                 | 5 min       | 61           | 12 : 1                |
| 14.   | BnO-CHOH       | 5 min       | 79          | 6 : 1                  | 20 min      | 83           | 6 : 1                 |

(a) Isolated yields
(b) Anomeric ratio is determined by $^1$H-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)$_3$-SiO$_2$ reagents is presented in Table 2. Although BiCl$_3$ 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 %                |
|       |         | BiCl₃                  | 1 h    | 94        | 10 : 1        | 5 mol%                  |
|       |         | InCl₃                  | 10 min | 86        | 6.3 : 1       | 20 mol %                |
|       |         | Bi(OTf)₃-SiO₂         | 15 min | 90        | 2.2 : 1       | 2 mol %                 |
|       |         | Bi(OTf)₃              | 3 min  | 69        | 4 : 1         | 2 mol %                 |
| 2.    | Ph−OH   | CAN                    | 2.5 h  | 89        | 9 : 1         | 10 mol %                |
|       |         | Sc(OTf)₃              | 2.5 h  | 92        | 9 : 1         | 5 mol %                 |
|       |         | Bi(OTf)₃-SiO₂         | 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 %                |
|       |         | BiCl₃                  | 1.5 h  | 95        | 10 : 1        | 5 mol %                 |
|       |         | Bi(OTf)₃-SiO₂         | 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 %                 |
|       |         | BiCl₃                  | 1.5 h  | 95        | 11 : 1        | 5 mol %                 |
|       |         | Bi(OTf)₃-SiO₂         | 2 h    | 51        | α             | 2 mol %                 |
|       |         | Bi(OTf)₃              | 3 min  | 75        | α             | 2 mol %                 |
|       |         | I₂                     | 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 %                |
|       |         | InCl₃                  | 30 min | 90        | 9 : 1         | 20 mol %                |
|       |         | Bi(OTf)₃              | 30 min | 82        | α             | 2 mol %                 |
|       |         | Bi(OTf)₃-SiO₂         | 2 h    | 80        | 3 : 1         | 2 mol %                 |
| 6.    | BnO−OH  | 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-SiO₂         | 20 min | 83        | 6 : 1         | 2 mol %                 |
| 7.    | Cholesterol | CAN           | 5 h    | 78        | 10 : 1        | 10 mol %                |
|       |         | BiCl₃                  | 2 h    | 90        | 4 : 1         | 5 mol %                 |
|       |         | Bi(OTf)₃              | 2 h    | 70        | α             | 2 mol %                 |
|       |         | Bi(OTf)₃-SiO₂         | 3 h    | 74        | 15 : 1        | 2 mol %                 |
Likewise, with allyl alcohol, propargyl alcohol and cholesterol (entry 7) the Ferrier product is a mixture of \( \alpha \) and \( \beta \) anomers using bismuth chloride whereas with Bi(OTf)\(_3\) only the \( \alpha \) anomer is obtained. In general, the amount of the BiCl\(_3\) used is 5 mol\%, whereas Bi(OTf)\(_3\) is used in only 2 mol\% indicating that it is more reactive than BiCl\(_3\). Thus, overall it appears that Bi(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 furandiol 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 furandiol 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 Pd(OAc)\(_2\), RuCl\(_2\)(PPh)\(_3\), Sm(OTf)\(_3\) and Yb(OTf)\(_3\) for the transformation of 3 into 4, reporting yields ranging from 44% to 70% and requiring 30-165 minutes at 80-100\(^\circ\)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 InCl\(_3\)-3H\(_2\)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 Bi(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 Bi(OTf)\(_3\) and it took 5 minutes for the reaction to complete, resulting in a 47% yield of the diol 4.

**Scheme 2**

\[
\text{HO} \quad \text{Bi(O Tf)\(_3\) or} \quad \text{Bi(O Tf)\(_3\)-SiO\(_2\)} \quad \text{CH}_3\text{CN} \quad \text{Bi(O Tf)\(_3\)-SiO\(_2\)} \quad \text{OH}
\]

**Conclusions**

We have developed a highly stereoselective, Bi(OTf)\(_3\) and SiO\(_2\)-Bi(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.

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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. CH$_3$CN was dried over P$_2$O$_5$ followed by over CaH$_2$. After distillation it was stored over 4Å molecular sieves and used directly for the reactions. Dichloromethane was dried over anhydrous CaCl$_2$ and freshly distilled over CaH$_2$ 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 CDCl$_3$ as the solvent. The yields reported are after purification. All compounds are known and the structures were confirmed by $^1$H-NMR and $^{13}$C-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 CH$_3$CN (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-\(\text{O-}\)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 NaHCO$_3$ 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 Na$_2$SO$_4$. Pure compound was obtained by column chromatography on SiO$_2$ (100-200 mesh).

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

\[ \text{AcO} \quad \text{O} \quad \text{Ac} \]

$^1$H-NMR (400 MHz, CDCl$_3$) (\(\alpha\)-anomer) $\delta$: 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). ($\beta$-anomer) $\delta$: 8.34 (s, 1H), 6.11 (brs, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$) (\(\alpha\)-anomer) $\delta$: 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(CH$_2$Cl$_2$) v: 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: $^1$H-NMR (400 MHz, CDCl$_3$) (\(\alpha\)-anomer) $\delta$: 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, CDCl₃) ($\alpha$-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 (CH₂Cl₂) ν: 3055, 1740, 1232, 739 cm⁻¹. MSES⁺: 819 [2M+Na]⁺, 421 [M+Na]⁺.

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