Bismuth Triflate: An Efficient Catalyst for the Formation and Deprotection of Tetrahydropyranyl Ethers

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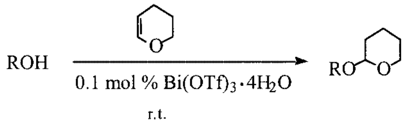
The tetrahydropyranylation of alcohols under solvent-free conditions is efficiently catalyzed by bismuth triflate (0.1 mol %). The experimental procedure is simple and works well with a variety of alcohols and phenols. The catalyst is insensitive to air and small amounts of moisture, easy to handle and relatively nontoxic. The deprotection of THP ethers is also catalyzed by bismuth triflate (1.0 mol %).

Introduction

A common and useful protecting group for alcohols and phenols is tetrahydropyranyl (THP) ether.[1] THP ethers are stable under a variety of reaction conditions such as strongly basic media, hydrides, acylating agents and alkylating agents. Several reagents have been developed as catalysts for the formation of THP ethers from alcohols and dihydropyran. These include *p*-TsOH,[2] pyridinium *p*-toluenesulfonate (PPTS),[3] Amberlyst H-15,[4] $(TMSO)_2SO_2$,[5] TMSI,[6] Nafion-H,[7] K-10 montmorillonite,[8] Reillex®,[9] $Ph_3P{\cdot}HBr$,[10] ceric ammonium nitrate,[11] H-Y zeolite,[12] sepiolite clay,[13] $ZnCl_2$,[14] heteropoly acids,[15] $CuCl_2$,[16] $LiClO_4$ in diethyl ether,[17] LiBr in CH_2Cl_2,[18] Zeolite H-beta,[19] and $K_5CoW_{12}O_{40}{\cdot}3H_2O$.[20] Many of these methods require the use of a corrosive reagent, and the reaction is usually done in a solvent. Few of these methods report the formation of THP ethers from tertiary alcohols.[3,5,8,10,12] Thus, in spite of a number of existing methods for the formation of THP ethers, the development of new methods which utilize highly catalytic, versatile and easy to handle reagents is desirable. Due to our continued interest in bismuth compounds, we investigated the utility of bismuth triflate as a catalyst for the conversion of alcohols and phenols to the corresponding THP ethers as well as their subsequent deprotection. Bismuth compounds have recently attracted attention due to their low cost, ease of handling and remarkably low toxicity.[21,22] We now report that bismuth triflate, $Bi(CF_3SO_3)_3{\cdot}4H_2O$ (0.1−1.0 mol %) is an efficient and versatile catalyst that can be used for both the conversion of alcohols to THP ethers and for the deprotection of THP ethers. Bismuth triflate has previously been used as a catalyst for Friedel−Crafts acylations,[23] sulfonylation of arenes,[24] Diels−Alder reactions,[25] aza-Diels−Alder reactions,[26] the rearrangement of epoxides,[27] the formation of acylals,[28] and the deprotection and formation of acetals.[29]

Bismuth triflate is a highly efficient catalyst for the formation of THP ethers under solvent-free conditions (Scheme 1). Bismuth triflate is not commercially available but can be easily synthesized in large quantities in the laboratory.[30]



Scheme 1

The experimental procedure is very simple and involves stirring of the alcohol and dihydropyran in a flame-dried flask under N_2 at room temperature. The product is isolated by filtration through a column of basic alumina. The results of this study are summarized in Table 1.

For substrates that are solids or are not very soluble in DHP (Entries 10, 18), the reaction was carried out in CH_2Cl_2. The procedure works with a variety of primary, secondary, tertiary and allylic alcohols as well as with diols and phenols. It is noteworthy that in the case of tertiary alcohols (Entries 12−15), no dehydration product was observed. The attempt to form the mono-THP ether from 1,5-pentanediol (Entry 3) was not successful. The use of 1.1 equiv. of dihydropyran gave a mixture of mono- and bis(THP ether)s along with unchanged starting material. However, the use of 2.5 equiv. of dihydropyran afforded the bis(THP ether) in good yield. The procedure is mild enough to tolerate several other functional groups, such as a triple

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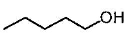
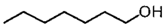
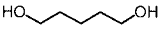
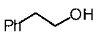
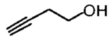
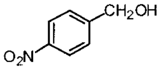
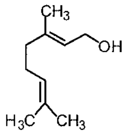
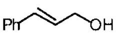
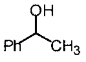
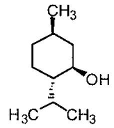
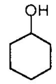
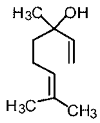
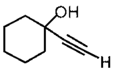
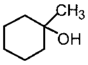
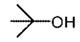
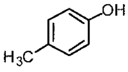
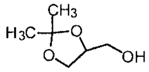
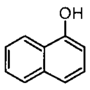
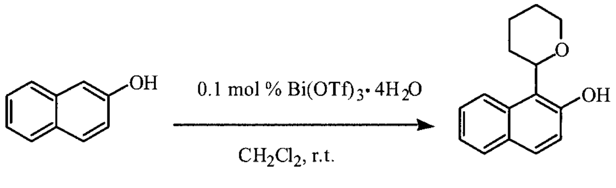
Table 1. Formation of THP ethers from alcohols and phenols using $Bi(CF_3SO_3)_3·4H_2O$

Entry[a]	Substrate	Time[b]	Yield of THP ether[c]	^{13}C NMR spectral data
1[38]		3.5 h	87%	13.9, 19.6, 22.5, 25.4, 28.4, 29.4, 30.7, 62.2, 67.6, 98.7
2[20]		1.5 h	75%	14.0, 19.6, 22.6, 25.5, 26.2, 29.1, 29.7, 30.7, 31.8, 62.2, 67.6, 98.8
3[38]		6.25 h[d]	70%	19.4, 22.7, 25.3, 29.3, 30.5, 61.9, 67.2, 98.5
4[39]		1 h	82%	19.3, 25.3, 30.5, 36.2, 62.0, 68.1, 98.5, 126.0, 128.1, 128.8, 138.9
5[40]		30 min	75%	19.2, 19.8, 25.3, 30.4, 62.0, 65.3, 69.1, 81.2, 98.5
6[41]		4 h	85%	19.1, 25.2, 30.3, 62.1, 67.5, 98.1, 123.4, 127.6, 146.0, 147
7[4]		2 h	83%	16.4, 17.7, 19.7, 25.6, 25.7, 26.4, 30.8, 39.7, 62.2, 63.6, 97.7, 120.7, 124.2, 131.5, 140.2
8[36]		4 h	86%	19.3, 25.3, 30.4, 62.0, 67.4, 97.6, 125.8, 126.3, 127.4, 128.3, 132.1, 136.6
9[8]		1 h	63%[h]	18.9. 19.6, 19.7, 24.1, 25.3, 30.6, 61.7, 62.5, 72.8, 72.9,95.8, 95.9, 125.7, 126.2, 126.7, 127.1, 127.9, 128.1, 143.4, 144.2
10[4,44]		2 h[e]	74%[h]	—
11[8]		3.25 h	83%	19.9, 24.0, 24.3, 25.4, 25.6, 31.2, 31.6, 33.6, 62.5, 74.2, 96.4
12[10]		25 h[f]	74%[h]	17.5, 20.46, 20.54, 22.4, 22.5, 22.7, 23.5, 25.4, 25.6, 32.2, 32.4, 40.1, 41.7, 63.0, 63.2, 78.3, 78.5, 94.1, 94.4, 113.3, 114.3, 124.5, 131.1, 143.1, 143.6
13[42]		3 h	75%	20.3, 22.8, 25.1, 25.3, 31.9, 38.3, 38.5, 63.3, 73.8, 74.6, 85.2, 95.5
14[39]		21 h	84%	20.8, 22.8, 22.3, 25.4, 25.7, 26.1, 32.6, 36.4, 38.2, 63.4, 75.0, 93.4
15[43]		22.5 h	75%	20.9, 25.3, 28.6, 32.4, 63.4, 74.1, 94.2
16[4]		2 h	80%	18.7, 20.4, 25.2, 30.3, 61.8, 96.4, 116.3, 129.7, 130.7, 154.8
17[39]		3.25 h	78%[h]	19.2, 19.3, 25.2, 25.3, 25.4, 26.56, 26.63, 30.3, 61.9, 62.1, 66.6, 66.8, 67.8, 68.4, 74.6, 74.7, 98.8, 99.0, 109.1, 109.3
18[39]		4 h[e,g]	64%	18.7, 25.2, 30.4, 61.8, 96.1, 108.1, 120.9, 121.9, 125.1, 125.9 (2 peaks), 126.1, 127.5, 134.5. 152.4

[a] Superscript number against entry refers to literature reference for the THP ether. All THP ethers have been previously reported. However, the ^{13}C NMR spectroscopic data for most of these compounds has not been reported previously and, hence, they are listed here. [b] Reaction progress was monitored by TLC, GC, IR and/or NMR analysis. [c] Refers to yield of isolated, purified product. All products were ≥ 97% pure. Purity was determined by ^1H NMR, ^{13}C NMR and GC. Some THP ethers decomposed on the GC column. [d] Product is bis(tetrahydropyranyl ether). 2.5 equiv. of DHP used. [e] Reaction was carried out in CH_2Cl_2. [f] 1.8 equiv. of DHP used. [g] 2.6 equiv. of DHP used. [h] Obtained as a mixture of diastereomers.

bond (Entries 5 and 13), allylic alcohols (Entries 7 and 8), and acetonides (Entry 17).

The conversion of 1-naphthol (Entry 18) to the corresponding THP ether was successfully carried out in CH_2Cl_2 as the solvent. Although the formation of the THP ether of 2-naphthol has been reported in the literature using catalysts such as LiBr in CH_2Cl_2 [18] and zeolite H-beta,[19] the use of bismuth triflate as a catalyst did not afford the corresponding THP ether. Instead, smooth C-alkylation to afford the hydroxy ether **20** was observed (Scheme 2). We obtained similar results using concentrated HCl as the catalyst. The identity of the product was confirmed by analysis of its IR, ^1H and ^{13}C NMR spectra.[31]

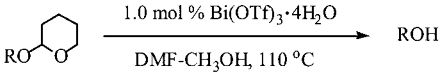


19 **20**

Scheme 2

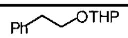
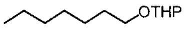
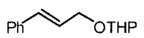
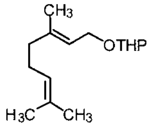
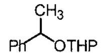
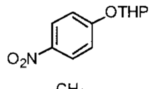
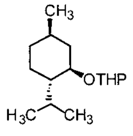
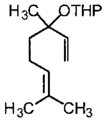
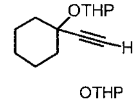
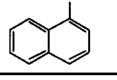
In order to determine the efficiency of various metal triflates in catalyzing the tetrahydropyranylation of alcohols, the reaction of cinnamyl alcohol with dihydropyran was carried out using 0.1 mol % of $Bi(OTf)_3·4H_2O$, $La(OTf)_3$, $In(OTf)_3$, and $Yb(OTf)_3·xH_2O$. All of these reactions were carried out with 1.0 g of cinnamyl alcohol (Entry 8, Table 1) under solvent-free conditions for 4 h and the product was isolated by filtration of the reaction mixture through a column of silica gel. In addition to the metal triflates, the tetrahydropyranylation was attempted with *p*-TsOH and triflic acid. The yield of the corresponding THP ether (75−85%) was similar to that with all the triflates, as well as 0.1 mol % of *p*-TsOH and triflic acid. However, of all the catalysts, bismuth triflate proved to be the most convenient and practical, since it is easy to handle and weigh out without the need for a dry atmosphere. Triflic acid and *p*-TsOH, due to their corrosive nature, are especially difficult to handle. The observation that triflic acid catalyzes these reactions suggests that it is possibly an active catalyst in case of the metal triflates as well.

Several methods are reported in the literature for the deprotection of THP ethers to the corresponding alcohols. Some recent examples include DDQ in wet CH_3CN,[32] LiCl in H_2O/DMSO,[33] CBr_4/CH_3OH,[34] ceric ammonium nitrate,[35] $CuCl_2{\cdot}2H_2O$ in CH_3OH,[36] and $Sc(OTf)_3$ (5 mol %).[37] We now report that the deprotection of THP ethers under non-aqueous conditions (Scheme 3) is also catalyzed by bismuth triflate (1.0 mol %). The best results were obtained using DMF/CH_3OH (9:1, v/v) as the solvent system. The results of the deprotection of THP ethers are summarized in Table 2.



Scheme 3

Table 2. Deprotection of THP ethers catalyzed by $Bi(OTf)_3{\cdot}4H_2O$ in DMF/CH_3OH (9:1)

Entry	Substrate	Time	Yield of alcohol[a]
1		13 h	71%
2		24 h	67%
3		15 h	84%
4		40 h	81%
5		15 h	80%
6		6 h	89%
7		26 h	83%
8		22 h	79%
9		19 h	84%
10		20 h	85%

[a] Refers to yield of isolated, purified product.

In summary, bismuth triflate is a versatile catalyst for both protection and deprotection of THP ethers. The low toxicity and ease of handling of the reagent make it an attractive alternative to existing reagents for formation of THP ethers.

Experimental Section

General: NMR spectra were recorded with a JEOL Eclipse NMR spectrometer at 270 MHz (^1H) and 67.5 MHz (^{13}C) in $CDCl_3$ as the solvent. Flash chromatography for the purification of alcohols and phenols was performed on Merck silica gel (230−400 mesh) and on basic alumina or silica gel for THP ethers. Thin-layer chromatography was performed on aluminum-backed silica gel plates. Spots were visualized under UV light and by spraying the plate with phosphomolybdic acid, followed by heating. Dihydropyran was dried with solid NaOH and then distilled under nitrogen. All products have been reported previously in the literature and were characterized by ^1H, ^{13}C NMR and IR spectroscopy. Purity was further checked by means of GC analysis using a Varian CP 3800 capillary GC. A few THP ethers did not survive the GC analysis.

General Procedure for the Tetrahydropyranylation of Alcohols under Solvent-Free Conditions: A solution of 1-pentanol (2.00 g, 22.7 mmol) and 3,4-dihydro-2*H*-pyran (2.69 mL, 29.50 mmol, 1.3 equiv.) was stirred in a flame-dried three-necked flask under N_2 as $Bi(OTf)_3{\cdot}4H_2O$ (14.9 mg, 0.023 mmol, 0.1 mol %) was added. The solution turned faint yellow and became slightly warm. After 3.5 h, the crude product was filtered through 60 g of basic alumina using ethyl acetate/hexane (15:85) as the eluent to afford 3.39 g (87%) of 1-pentanol THP ether as a colorless liquid. The product was characterized by IR, ^1H and ^{13}C NMR spectroscopy.

General Procedure for the Tetrahydropyranylation of Alcohols in CH_2Cl_2: A solution of (−)-(1*R*,2*S*,5*R*)-menthol (1.00 g, 6.40 mmol) and dihydropyran (0.76 mL, 8.32 mmol, 1.3 equiv.) in CH_2Cl_2 (10 mL) was stirred as $Bi(OTf)_3{\cdot}4H_2O$ (4.2 mg, 0.0064 mmol, 0.1 mol %) was added. After 10 min, the reaction mixture turned pale yellow and became slightly warm. The mixture was stirred for 2 h, and then additional CH_2Cl_2 (20 mL) was added. The mixture was washed with 10% $NaHCO_3$ (20 mL), H_2O (4 × 15 mL), saturated NaCl (15 mL), and dried (Na_2SO_4). The solvent was removed in a rotary evaporator to yield 1.498 g of a clear, pale yellow liquid. A portion of the crude material (0.82 g) was purified flash chromatography on 50 g of basic alumina to yield 0.62 g (74% overall yield) of the corresponding THP ether as a mixture of diastereomers. The product was characterized by IR, ^1H and ^{13}C NMR spectroscopy.

General Procedure for the Tetrahydropyranylation of Phenols in CH_2Cl_2: A solution of 1-naphthol (4.06 g, 28.2 mmol) and dihydropyran (6.16 g, 6.68 mL, 73.2 mmol, 2.6 equivalents) in CH_2Cl_2 (40 mL) was stirred in a flame-dried round-bottom flask at room temperature under N_2 as $Bi(OTf)_3{\cdot}4H_2O$ (18.5 mg, 0.028 mmol, 0.1 mol %) was added. The resulting mixture was stirred at room temperature for 4 h and diluted with CH_2Cl_2 (25 mL). The mixture was washed with aqueous 3 M NaOH solution (30 mL), saturated NaCl (20 mL) and dried (Na_2SO_4). The solvent was removed in a rotary evaporator to yield 6.15 g of an oil that was purified by flash chromatography on 120 g of silica gel using hexane/CH_2Cl_2 (7:3, v/v) as the eluent to afford 4.10 g (64%) of a pale yellow oil. The product was identified as the corresponding THP ether by ^{1}H, ^{13}C NMR and IR spectroscopy.

General Procedure for the Deprotection of THP Ethers:[45] Bismuth triflate in methanol has been reported as a catalyst for the deprotection of THP ethers. In our hands, this method did not give reproducible results. A solution of the THP ether of *sec*-phenethyl alcohol (mixture of diastereomers, 1.618 g, 7.844 mmol) in DMF/CH$_3$OH (16.0 mL, 9:1, v/v) was stirred at room temperature as Bi(OTf)$_3$·4H$_2$O (51.47 mg, 0.07844 mmol, 1.0 mol %) was added. The resulting mixture was heated in an oil bath at 110 °C for 15 h and then cooled to room temperature. Aqueous 10% NaHCO$_3$ (10 mL) was added, and the mixture was stirred thoroughly. The mixture was extracted with ether (2 × 25 mL) and the organic layer was washed with H$_2$O (4 × 10 mL), aqueous saturated NaCl (15 mL) and dried (Na$_2$SO$_4$). The solvents were removed in a rotary evaporator to yield 0.9520 g of a liquid that was purified by flash chromatography on 45 g of silica gel using ethyl acetate/hexane (20:80, v/v) as the eluent to afford 0.7670 g (80%) of a colorless oil that was identified as *sec*-phenethyl alcohol. The purity of the product as determined to be greater than 98% by ^{1}H and ^{13}C NMR spectroscopy and GC analysis.

Acknowledgments

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