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Efficient and Selective Conversion of Trimethylsilyl and Tetrahydropyranyl Ethers to their Corresponding Acetates and Benzoates Catalyzed by Bismuth(III) Salts

Iraj Mohammadpoor-Baltork* and **Ahmad R. Khosropour**

Department of Chemistry, Isfahan University, Isfahan 81744, Iran

Summary. A variety of *TMS* and *THP* ethers are efficiently converted to their corresponding acetates and benzoates with acetic and benzoic anhydrides in the presence of catalytic amounts of Bi(III) salts such as $BiCl_3$, Bi(*TFA*)$_3$, and Bi(O*Tf*)$_3$. The present method is also effective for the selective acetylation and benzoylation of *TMS* and *THP* ethers of alcohols in the presence of phenolic ethers.

Keywords. Acylation; Alcohols; Phenols; Bi(III) salts; *Lewis* acids.

Introduction

Esterification is an important and well-established reaction in organic synthesis. Esters are useful as solvents, artificial flavours, and essences; They are usually prepared by esterification of carboxylic acids [1–3], transesterification [4], alkylation of carboxylate anions [5], acylation of alcohols and phenols [6–13], or cleavage of ethers [14]. However, little attention has been paid to the esterification of trimethylsilyl (*TMS*) and tetrahydropyranyl (*THP*) ethers, and only a few reports are available dealing with the conversion of these ethers to their corresponding esters [15]. Therefore, the introduction of new methods and catalysts for the esterification of *TMS* and *THP* ethers is of value in synthetic organic chemistry.

The application of bismuth compounds as catalysts in organic transformations has been investigated extensively [16]. In the course of our research on catalysis by Bi(III) salts [17] and also on reactions of *TMS* and *THP* ethers [18], we now report a simple, efficient and selective method for the conversion of *TMS* and *THP* ethers to their corresponding acetates and benzoates using $BiCl_3$, Bi(*TFA*)$_3$, and Bi(O*Tf*)$_3$ as catalysts (Scheme 1).

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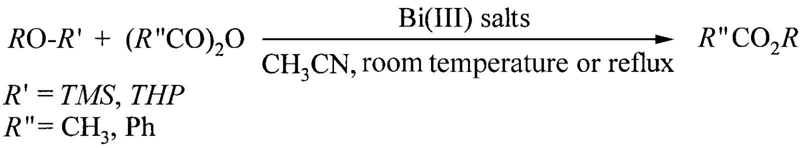
* Corresponding author. E-mail: imbaltork@sci.ui.ac.ir



$$RO\text{-}R' + (R''CO)_2O \xrightarrow[\text{CH}_3\text{CN, room temperature or reflux}]{\text{Bi(III) salts}} R''CO_2R$$

$R' = TMS, THP$
$R'' = CH_3$, Ph

Scheme 1

Results and Discussion

As shown in Table 1, a series of *TMS* ethers were treated with acetic and benzoic anhydrides under catalysis by $BiCl_3$, Bi(*TFA*)$_3$, and Bi(O*Tf*)$_3$ in acetonitrile at room temperature or under reflux to afford the corresponding acetates and benzoates in excellent yields.

The acetylation and benzoylation of *THP* ethers were also investigated. The treatment of a variety of *THP* ethers with acetic and benzoic anhydrides in the presence of catalytic amounts of $BiCl_3$, Bi(*TFA*)$_3$, or Bi(O*Tf*)$_3$ in refluxing acetonitrile provided the corresponding acetates and benzoates in good to excellent yields (Table 2). The experimental results show that Bi(O*Tf*)$_3$ is more reactive than $BiCl_3$ and Bi(*TFA*)$_3$ and works better in terms of reaction times and yields.

In order to explore further the synthetic utility of this procedure, the competitive acetylation and benzoylation of *TMS* and *THP* ethers of alcohols and phenols were also investigated. As shown in Table 3, *TMS* and *THP* ethers of alcohols are converted to their corresponding acetates and benzoates in the

Table 1. Conversion of *TMS* ethers to their corresponding acetates and benzoates in the presence of Bi(III) salts[a]

TMS ether	Yield of acetate/%[b] (*t*/min)			Yield of benzoate/%[b] (*t*/min)		
	$BiCl_3$[c]	Bi(*TFA*)$_3$[c]	Bi(O*Tf*)$_3$[d]	$BiCl_3$[c]	Bi(*TFA*)$_3$[c]	Bi(O*Tf*)$_3$[c]
$C_6H_5CH_2CH_2O$*TMS*	98 (20)	97 (20)	99 (15)	98 (60)	98 (60)	99 (45)
$C_6H_5CH_2CH_2CH_2O$*TMS*	96 (20)	95 (20)	98 (15)	94 (30)	94 (30)	97 (30)
2-$MeOC_6H_4CH_2O$*TMS*	95 (30)	90 (30)	98 (30)	97 (50)	80 (50)	97 (30)
3-$MeOC_6H_4CH_2O$*TMS*	97 (20)	96 (20)	97 (20)	98 (30)	97 (45)	98 (25)
4-$MeOC_6H_4CH_2O$*TMS*	96 (15)	95 (15)	97 (15)	98 (30)	97 (30)	99 (20)
3-$NO_2C_6H_4CH_2O$*TMS*	90 (35)	92 (35)[f]	94 (30)	85 (90)	90 (105)	95 (45)
4-$NO_2C_6H_4CH_2O$*TMS*	94 (40)	91 (40)[f]	97 (20)	89 (90)	90 (105)	97 (45)
4-$ClC_6H_4CH_2O$*TMS*	94 (30)	90 (30)	95 (30)	91 (60)	92 (60)	98 (30)
$C_6H_5CH(CH_3)O$*TMS*	95 (40)	94 (40)[f]	95 (35)	97 (60)	96 (60)	99 (45)
$CH_3(CH_2)_6O$*TMS*	96 (20)	95 (20)	97 (15)	93 (30)	95 (30)	95 (30)
$CH_3(CH_2)_7O$*TMS*	97 (20)	94 (20)	98 (15)	96 (30)	94 (30)	97 (30)
$C_6H_5COCH(C_6H_5)O$*TMS*	96 (30)	85 (45)[f]	97 (25)	82 (60)	80 (60)	94 (30)
4-ClC_6H_4O*TMS*	89 (60)[e]	87 (50)[f]	90 (30)[c]	85 (120)	85 (120)	93 (90)
α-NaphthylO*TMS*	90 (60)[e]	85 (45)[f]	92 (25)[c]	82 (105)	82 (120)	90 (90)
β-NaphthylO*TMS*	92 (60)[e]	90 (50)[f]	97 (25)[c]	85 (105)	80 (120)	95 (90)

[a] All products were identified by comparison of their physical and spectroscopic data with those of authentic samples; [b] isolated yields; [c] reaction performed under reflux; [d] reaction performed at room temperature; [e] 0.25 mmol of $BiCl_3$; [f] 0.15 mmol of Bi(*TFA*)$_3$

Table 2. Conversion of *THP* ethers to their corresponding acetates and benzoates in the presence of Bi(III) salts[a]

THP Ether	Yield of acetate/%[b] (*t*/min)			Yield of benzoate/%[b] (*t*/min)		
	$BiCl_3$	Bi(*TFA*)$_3$	Bi(O*Tf*)$_3$	$BiCl_3$	Bi(*TFA*)$_3$	Bi(O*Tf*)$_3$
$C_6H_5CH_2O$*THP*	92 (45)	90 (45)	95 (30)	85 (60)	83 (60)	90 (50)
$C_6H_5CH_2CH_2O$*THP*	90 (60)	91 (60)	93 (30)	82 (60)	80 (60)	91 (50)
$C_6H_5CH_2CH_2CH_2O$*THP*	82 (50)	85 (50)	95 (30)	89 (60)	91 (60)	94 (50)
3-$MeOC_6H_4CH_2O$*THP*	85 (70)	80 (70)	90 (45)	85 (80)	88 (80)	93 (50)
4-$MeOC_6H_4CH_2O$*THP*	90 (60)	90 (60)	95 (30)	84 (75)	85 (75)	90 (50)
2-$NO_2C_6H_4CH_2O$*THP*	82 (100)	84 (100)	85 (45)	80 (120)	82 (120)	86 (60)
4-$NO_2C_6H_4CH_2O$*THP*	85 (70)	82 (70)	95 (40)	81 (100)	80 (100)	95 (60)
$PhCH(CH_3)O$*THP*	85 (60)	83 (60)	94 (45)	75 (120)	72 (120)	90 (60)
$CH_3(CH_2)_6O$*THP*	94 (45)	90 (45)	96 (35)	94 (45)	90 (45)	97 (35)
$CH_3(CH_2)_7O$*THP*	92 (45)	88 (45)	97 (35)	96 (45)	93 (45)	98 (35)
CyclohexylO*THP*	92 (45)	90 (50)	93 (30)	85 (45)	87 (45)	90 (35)
(–)-MenthylO*THP*[c]	85 (60)	83 (60)	87 (35)	87 (60)	84 (60)	90 (45)
2-$NO_2C_6H_4O$*THP*	75 (120)	72 (120)	80 (75)	65 (180)	64 (180)	75 (135)
β-NaphthylO*THP*	85 (120)	80 (120)	90 (50)	83 (180)	81 (180)	85 (120)

[a] All products were identified by comparison of their physical and spectroscopic data with those of authentic samples; [b] isolated yields; [c] (–)-menthylacetate and (–)-menthylbenzoate were obtained from the reaction mixture

presence of phenolic *TMS* and *THP* ethers with high selectivity. Such a selectivity has not been reported previously and can be considered as a useful practical achievement in esterification reactions.

In conclusion, we have demonstrated that $BiCl_3$, Bi(*TFA*)$_3$, and Bi(O*Tf*)$_3$ are practical and useful catalysts for the conversion of *TMS* and *THP* ethers to the corresponding acetates and benzoates. In addition, high yields, short reaction times, easy workup, availability, stability, and non-toxicity of the catalysts are noteworthy advantages of this method.

Experimental

Bi(*TFA*)$_3$ and Bi(O*Tf*)$_3$ were prepared according to Ref. [19].

General procedure for the conversion of TMS ethers to their corresponding acetates and benzoates

To a solution of 1 mmol *TMS* ether and 1.5 mmol acetic or benzoic anhydride in 3 cm^3 CH_3CN, the catalyst was added (in the case of acetic anhydride, 0.2–0.25 mmol of $BiCl_3$, 0.1–0.15 mmol of Bi(*TFA*)$_3$, or 0.03 mmol of Bi(O*Tf*)$_3$; in the case of benzoic anhydride, 0.25 mmol of $BiCl_3$, 0.2 mmol of Bi(*TFA*)$_3$, or 0.05 mmol of Bi(O*Tf*)$_3$). The reaction mixture was stirred at room temperature or under reflux for the time indicated in Table 1. The progress of the reaction was monitored by GLC or TLC. The solvent was evaporated, and 20 cm^3 ether were added. The reaction mixture was washed with 5% aqueous solution of $NaHCO_3$, then with H_2O, and dried over Na_2SO_4. Evaporation of the solvent followed by chromatography on silica gel (TLC or CC) afforded the pure product in 80–99% yield (Table 1).

Table 3. Competitive acetylation and benzoylation of *TMS* and *THP* ethers in the presence of Bi(III) salts

Substrate	Product	Yield/%^{a} (*t*/min)		
		BiCl_3	$\text{Bi}(\mathit{TFA})_3$	$\text{Bi}(\text{O}\mathit{Tf})_3$
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}\mathit{TMS}$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OAc}$	90 (40)	85 (40)	98 (20)
β-NaphthylO*TMS*	β-NaphthylOAc	5	10	0
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}\mathit{TMS}$	$\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OAc}$	90 (40)	85 (40)	98 (20)
$4\text{-ClC}_6\text{H}_4\text{O}\mathit{TMS}$	$4\text{-ClC}_6\text{H}_4\text{OAc}$	5	5	0
$\text{CH}_3(\text{CH}_2)_7\text{O}\mathit{TMS}$	$\text{CH}_3(\text{CH}_2)_7\text{OAc}$	95 (20)	93 (20)	100 (15)
β-NaphthylO*TMS*	β-NaphthylOAc	5	0	0
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}\mathit{TMS}$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OCOPh}$	70 (90)	75 (105)	90 (45)
β-NaphthylO*TMS*	β-NaphthylOCOPh	30	20	10
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}\mathit{TMS}$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OCOPh}$	82 (90)	85 (105)	94 (45)
$4\text{-ClC}_6\text{H}_4\text{O}\mathit{TMS}$	$4\text{-ClC}_6\text{H}_4\text{OCOPh}$	17	12	5
$\text{CH}_3(\text{CH}_2)_7\text{O}\mathit{TMS}$	$\text{CH}_3(\text{CH}_2)_7\text{OCOPh}$	89 (30)	95 (30)	98 (30)
β-NaphthylO*TMS*	β-NaphthylOCOPh	4	0	2
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}\mathit{THP}$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OAc}$	75 (70)	70 (70)	60 (40)
β-NaphthylO*THP*	β-NaphthylOAc	10	20	37
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}\mathit{THP}$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OAc}$	88 (70)	85 (70)	84 (40)
$2\text{-NO}_2\text{C}_6\text{H}_4\text{O}\mathit{THP}$	$2\text{-NO}_2\text{C}_6\text{H}_4\text{OAc}$	7	5	8
$\text{CH}_3(\text{CH}_2)_7\text{O}\mathit{THP}$	$\text{CH}_3(\text{CH}_2)_7\text{OAc}$	85 (45)	82 (45)	74 (35)
β-NaphthylO*THP*	β-NaphthylOAc	5	7	25
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}\mathit{THP}$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OCOPh}$	80 (100)	77 (100)	86 (60)
β-NaphthylO*THP*	β-NaphthylOCOPh	10	7	8
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}\mathit{THP}$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OCOPh}$	76 (100)	73 (100)	90 (60)
$2\text{-NO}_2\text{C}_6\text{H}_4\text{O}\mathit{THP}$	$2\text{-NO}_2\text{C}_6\text{H}_4\text{OCOPh}$	3	3	5
$\text{CH}_3(\text{CH}_2)_7\text{O}\mathit{THP}$	$\text{CH}_3(\text{CH}_2)_7\text{OCOPh}$	95 (45)	90 (45)	96 (35)
β-NaphthylO*THP*	β-NaphthylOCOPh	2	4	3

[a] GLC yield

General procedure for the conversion of THP ethers to their corresponding acetates and benzoates

A solution of 1 mmol *THP* ether and 1.5 mmol acetic or benzoic anhydride in 3 cm^3 CH_3CN was treated with the catalyst (in the case of acetic anhydride, 0.2 mmol of BiCl_3, 0.15 mmol of $\text{Bi}(\mathit{TFA})_3$, or 0.03 mmol of $\text{Bi}(\text{O}\mathit{Tf})_3$; in the case of benzoic anhydride, 0.3 mmol of BiCl_3, 0.25 mmol of $\text{Bi}(\mathit{TFA})_3$, or 0.06 mmol of $\text{Bi}(\text{O}\mathit{Tf})_3$). The reaction mixture was stirred under reflux for the time indicated in Table 2. The progress of the reaction was monitored by GLC or TLC. The solvent was evaporated, and 20 cm^3 ether were added. The reaction mixture was washed with 5% aqueous solution of NaHCO_3, then with H_2O, and dried over Na_2SO_4. Evaporation of the solvent followed by chromatography on silica gel (TLC or CC) provided the pure product in 64–98% yields (Table 2).

Acknowledgements

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