

Article

Mild and Highly Efficient Copper(I) Inspired Acylation of Alcohols and Polyols

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Abstract: A new and highly efficient method mediated by tetrakis(acetonitrile)copper(I) triflate for activating both simple and highly hindered anhydrides in the acylation of alcohols and polyols is described. This new acylation method is mild and mostly proceeds at room temperature with low catalyst loading. The method is versatile and has been extended to a wide variety of different alcohol substrates to afford the corresponding ester products in good to excellent yields.

Keywords: acylation; acetic anhydride; isobutyric anhydride; pivalic anhydride; polyols; copper(I) species

1. Introduction

The masking of hydroxyl groups to prevent side reactions during long synthetic reaction sequences continues to be of paramount importance in organic synthesis. These protection protocols usually involves the transformation of the hydroxyl groups to their corresponding ester analogs.

While the use of acetic anhydride, pyridine, and DMAP remains popular in transforming hydroxyl groups to the corresponding acetate esters [1], the noxious smell of pyridine as well as its high boiling point, makes its removal relatively difficult and can potentially complicate product isolation in synthetic protocols run on a small scale.

In an attempt to avoid the use of pyridine during the masking of hydroxyl groups, several alternative methods have been reported in recent years. Some notable methods include the use of I₂ [2–4], Br₂ [5] montmorillonite K-10 [6], FeCl₃ [7], TiCl₄-AgClO₄ [8], LiClO₄ [9], CuSO₄·5H₂O [10], TMSOTf [11], Bu₃P in CH₂Cl₂ [12,13], La(NO₃)₃·6H₂O [14], HClO₄-SiO₂ [15], molecular sieves [16], NaHCO₃ [17], Mg(NTf₂)₂ [18], 3-nitrobenzeneboronic acid [19], alumina [20], NBS [21], TaCl₅ [22], VO(OAc)₂ [23] and metal triflates such as Pd(PhCN)₂(OTf) [24], Cu(OTf)₂ [25], Bi(OTf)₂ [26], In(OTf)₂ [27,28], Sc(OTf)₂ [29], Ce(OTf)₂ [30], and CoCl₂ [31,32].

While all these methods provide a viable alternative in the acetylation of alcohols, long reaction times, high temperature requirements, and high catalyst loading required in some of these protocols has necessitated the need for the development of a new method of protecting hydroxyl groups to complement the existing methods.

In recent years, the use of copper(I) species as efficient catalysts in various cross-coupling reactions in the formation of C–C, C–N, and C–O linkages during organic transformations, and in the synthesis of natural products, has received considerable attention. Sharpless et al. as well as the Meldal research group independently employed the use of copper(I) catalysis in the formation of a cyclic adduct during azide-alkyne cycloaddition reactions [33,34]. In the synthesis of (–)-galbulimima alkaloid, the Movassaghi research group reported the use of copper-inspired coupling of vinyl bromide and oxazolidinone as one of its key intermediate steps [35]. A similar strategy was also employed in the synthesis of himandrine alkaloid [36]. Bergman et al. also reported the use of copper catalyzed

amidation reactions as one of its key strategies in the synthesis of the alkaloid vasicoline [37]. Again, Buchwald et al. also reported a domino Cu(I) catalyzed amidation/nucleophilic substitution protocol to access substituted indolines, a very important and common structural motif in many bioactive natural products [38].

In spite of the extensive use of copper-mediated catalysis in natural product synthesis, the use of copper(I) species in activating both simple and hindered anhydrides towards the masking of various hydroxyl groups in organic synthesis have not been investigated. We herein report a new, mild, and simple protocol that utilizes tetrakis(acetonitrile)copper(I) triflate as a highly efficient catalyst in the acylation of simple alcohols and polyols.

2. Results and Discussion

After an extensive preliminary study using a simple alcohol such as phenol **1** (1 equivalent) as the model substrate and acetic anhydride (4 equivalents) as the acetylation agent, we found that 1 mol % of tetrakis(acetonitrile)copper(I) triflate was able to efficiently catalyze the transformation of phenol **1** to the corresponding phenyl acetate **2** in 3 min and in quantitative yield.

This remarkable and rapid transformation of phenol **1** to its corresponding phenyl acetate **2** at low catalyst loading was very significant and may suggest the high capacity of copper(I) species to activate simple anhydrides towards the masking of hydroxyl groups. As a result of the excellent initial results with phenol, the versatility and efficacy of tetrakis(acetonitrile)copper(I) triflate was also explored using a variety of different alcohols as substrates and with acetic anhydride as the acetylating agent (Table 1).

Table 1. Acetylation of alcohols with acetic anhydride catalyzed by $\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf}$.

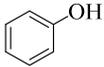
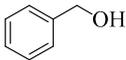
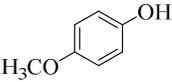
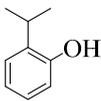
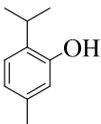
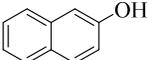
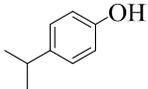
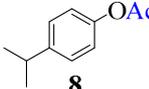
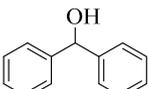
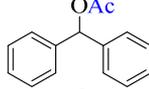
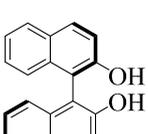
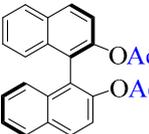
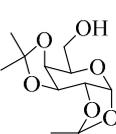
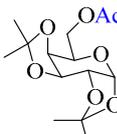
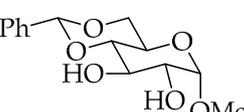
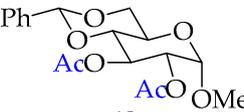
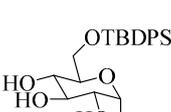
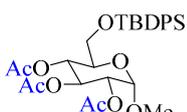
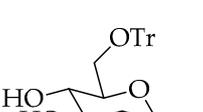
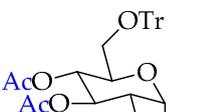
ROH (1 equiv.)		+	Ac_2O^a	$\xrightarrow[\text{rt, 3min - 1hr}]{\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf (1 mol%)}}$	ROAc
Entry	Substrate			Time (min)	Yield (%) ^b
1				3	98
	1			2	
2				20	91
				3	
3				30	94
				4	
4				30	90
				5	
5				45	89
				6	
6				22	92
				7	

Table 1. Cont.

		$\text{ROH (1 equiv.)} + \text{Ac}_2\text{O}^a \xrightarrow[\text{rt, 3min - 1hr}]{\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf (1 mol\%)} } \text{ROAc}$		
Entry	Substrate	Product	Time (min)	Yield (%) ^b
7			30	92
8			55	93
9			60	83
10			60	87
11			45	90
12			35	90
13			60	83
14			45	89

^a Reactions were carried out using 4 equiv. of acetic anhydride per hydroxyl group; ^b Isolated yield.

In all instances, there were smooth conversion to their corresponding esters **3–8** in excellent yields and in short reaction times (Table 1, Entries 2–7).

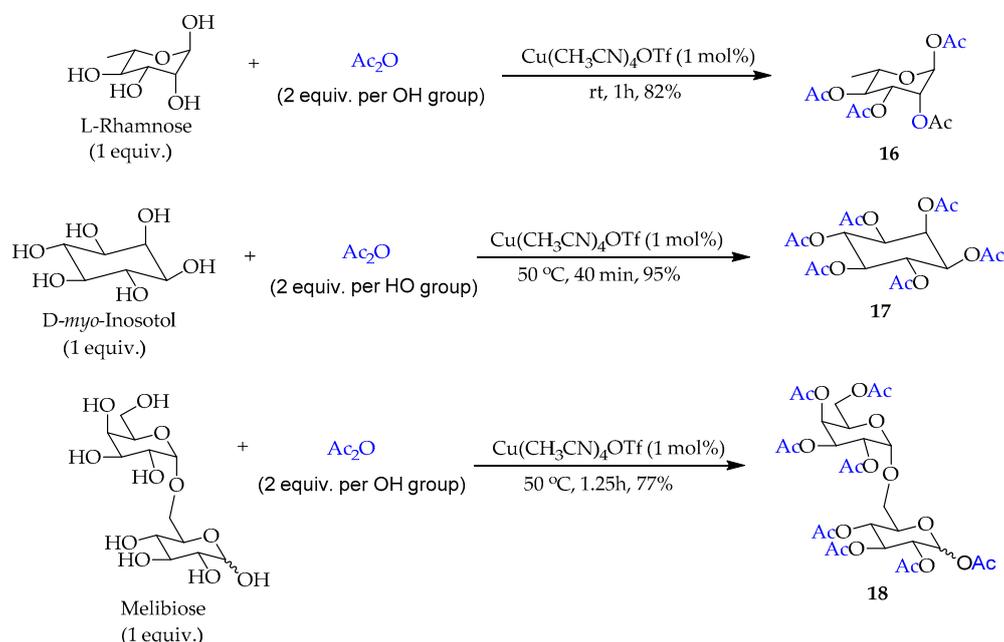
With these encouraging results, the efficacy of the Cu(I)catalyst in the presence of highly hindered alcohol substrates was also explored. In this study, the acetylation reaction was performed using highly hindered alcohol substrates such as diphenyl methanol and adamantanol (Table 1, Entries 8–9). Remarkably, there was a facile transformation of these hindered alcohols to their corresponding esters **9** and **10** respectively in excellent yields.

Since several acid labile hydroxyl-protecting groups are routinely employed in organic synthesis during long synthetic reaction sequences, the efficacy of this new acetylation protocol was also investigated in the presence of other acid labile hydroxyl-protecting groups. Using the acetonide protected galactose as a substrate, remarkably, the acid labile acetonide group survived this new reaction protocol, affording the corresponding protected galactose ester **12** in excellent yield (Table 1, Entry 11).

In the synthesis of oligosaccharides, functionalization of the monosaccharide units prior to their assembly is usually crucial. One of the main synthetic strategies used to achieve this objective is to employ the use of acid labile benzylidene acetal as a protecting group. This acid labile benzylidene acetal is routinely used to mask diols in a 1,2 and 1,3 configuration [39,40]. The tolerance of the acid sensitive benzylidene acetal to this acetylation protocol was also investigated using a benzylidene acetal protected glucose diol as the substrate. Gratifyingly, the acid labile benzylidene acetal-protecting group survived, affording the fully protected sugar **13** in excellent yield (Table 1, Entry 12).

To further explore the scope and generality of this acetylation protocol, the efficacy of the Cu(I) catalyst was also explored in the presence of a silyl- and trityl-protecting groups. Silyl- and trityl-protecting groups are among the most common hydroxyl-protecting groups used in organic synthesis. When silyl and trityl protected sugars were used as substrates, again, both protecting groups survived, affording fully acetylated sugars **14** and **15** respectively in excellent yields. (Table 1, Entries 13 and 14). All these results may suggest that this new Cu(I)-inspired acetylation protocol is not only highly efficient but also mild as well.

In the formation of glycosidic linkages during the synthesis of polysaccharides, one of the initial steps usually involve the acetylation of the polyhydroxyl monosaccharides. To probe the limits of this new acetylation method, the versatility and efficacy of this protocol was again investigated by using polyols derived from both carbohydrates and non-carbohydrates as substrates (Scheme 1).

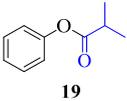
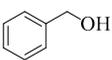
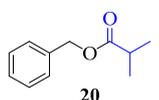
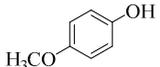
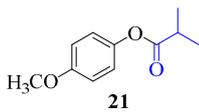
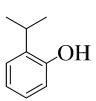
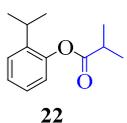
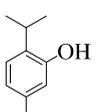
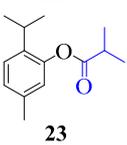
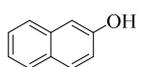
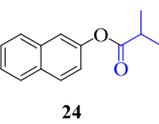
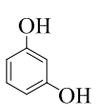
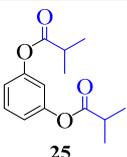
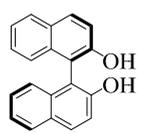
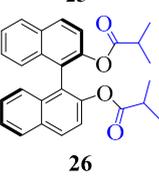
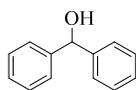
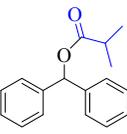


Using L-rhamnose sugar as substrate, the acetylation reaction proceeded with ease and at room temperature affording the fully acetylated sugar **16** in good yield (Scheme 1). With polyhydroxyl *myo*-inositol as substrate, the acetylation reaction was quite sluggish; however, upon warming up the reaction, the acetylation reaction proceeded smoothly to obtain the fully acetylated *D-my*o-inositol **17** in excellent yield (Scheme 1).

To continue exploring the scope and limits of this protocol, the Cu(I)-catalyzed acetylation reaction was again performed using a disaccharide-derived polyol such as melibiose as substrate. Although the reaction was also initially sluggish, upon warming the reaction to 50 °C, remarkably, there was a facile transformation of the polyol to the fully acetylated disaccharide **18** in good yield (Scheme 1).

As a result of the excellent versatility and efficacy of this catalyst, we again investigated the capacity of this catalyst in activating a relatively hindered acylating agent such as isobutyric anhydride in the acylation of alcohols (Table 2).

Table 2. Acylation of alcohols with isobutyric anhydride catalyzed by $\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf}$.

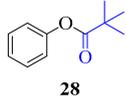
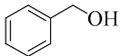
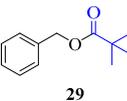
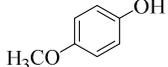
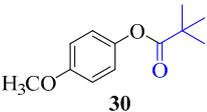
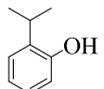
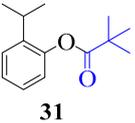
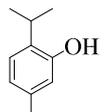
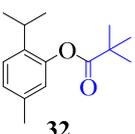
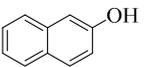
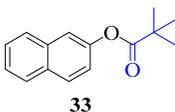
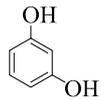
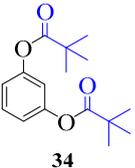
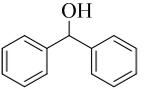
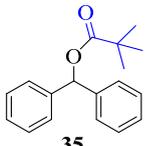
Entry	Substrate	Product	Time (min)	Yield (%) ^b
$\text{ROH (1 equiv.)} + \text{isobutyric anhydride} \xrightarrow[\text{rt, 15min - 3.5h}]{\text{Cu}(\text{CH}_3\text{CN})_4\text{OTf (1 mol\%)}} \text{RO-CO-CH(CH}_3)_2$				
1		 19	15	92
2		 20	180	93
3		 21	30	90
4		 22	60	93
5		 23	90	89
6		 24	60	91
7		 25	210	88
8		 26	90	85
9		 27	120	90

^a Reaction was carried out using 4 equiv. of isobutyric anhydride per hydroxyl group. ^b Isolated yield.

With phenol as the starting substrate and isobutyric anhydride as the acylation agent, the acylation reaction again proceeded smoothly with only 1 mol % catalyst loading, affording the phenyl isobutyrate **19** in excellent yield (Table 2, Entry 1). This exciting results prompted us to again investigate the scope of the catalyst using different alcohols with different steric encumbrance as substrate. In all cases, the acylation reaction afforded the corresponding acylated products **20–26** in excellent yields (Table 2, Entries 2–8). Remarkably, the acylation reaction again proceeded smoothly even with a hindered substrate such as diphenyl methanol at 1 mol % catalyst loading, affording the corresponding ester **27** in excellent yield (Table 2, Entry 9).

To further study the generality, scope, and efficiency of this new method of acylating alcohols, the capacity of Cu(I) catalysts to activate a highly hindered acylating agent such as pivalic anhydride was also investigated using different and sterically diverse alcohols as substrates (Table 3).

Table 3. Pivalation of alcohols catalyzed by Cu(CH₃CN)₄OTf.

Entry	Substrate	Product	Time (min)	Yield (%) ^b
$\text{ROH (1 equiv.)} + \text{Pivalic anhydride} \xrightarrow[\text{rt, 30min - 3.5h}]{\text{Cu(CH}_3\text{CN)}_4\text{OTf (1 mol\%)}} \text{RO-CO-C(CH}_3)_3$				
1		 28	30	90
2		 29	210	90
3		 30	30	93
4		 31	60	90
5		 32	90	86
6		 33	60	93
7		 34	50	86
8		 35	210	89

^a Reaction was carried out using 4 equiv. of pivalic anhydride per hydroxyl group; ^b Isolated yield.

It was gratifying to note that, in all cases using different alcohol substrates, the pivalation reaction proceeded with ease even with hindered substrates, transforming the alcohol substrates to the corresponding pivalate esters **28–35** in good to excellent yield.

These results are noteworthy because it demonstrates the capacity of Cu(I) catalyst tetrakis(acetonitrile)copper(I) triflate to activate both simple and highly hindered acid anhydrides towards the masking of hydroxyl groups.

While this protocol resulted in the facile transformation of the alcohols to the corresponding esters using different acylating agents, separating the fully acylated products from the excess isobutyric anhydride or pivalic anhydride used became problematic. To circumvent this problem, the methanolysis protocol reported by Otera et al. [26] was adopted and modified to decompose the excess isobutyric anhydride and pivalic anhydride.

To explore the origin of the observed catalysis, a control experiment with phenol as the substrate and acetic anhydride as the acylating agent was carried out in the absence of the Cu(I) catalyst. In this control reaction, there were no appreciable conversion of the phenol to the corresponding ester **2** even after stirring the reaction for 5 h. Similar results were also obtained when isobutyric anhydride and pivalic anhydrides were used as the acylating agents.

The lack of observable product formation obtained with phenol and acetic anhydride in the absence of the Cu(I) catalyst was in sharp contrast to the rapid acetylation of phenol in the presence of the catalyst (Table 1, Entry 1). Similarly, the results obtained during acylation of phenol when isobutyric anhydride and pivalic anhydride were used as the acylating agents in the presence of the Cu(I) catalyst (Table 2, Entry 1 and Table 3, Entry 1) were also in sharp contrast to the lack of product formation observed when the acylation reactions were carried out in the absence of the catalyst, which may suggest the crucial role of tetrakis(acetonitrile)copper(I) triflate in activating both simple and hindered anhydrides, thereby effecting the facile transformation of alcohols and polyols to their corresponding esters.

To further explore the source of the observed catalysis and the influence of the triflate counter ion, another control experiment was run with phenol as the substrate and acetic anhydride as the acylating agent. With 1 mol % triflic acid as the catalyst, the reaction was completed within 5 min to afford the phenyl acetate in a 90% yield. When the control experiment was repeated using a 1 mol % non-triflate Cu(I) source—Cu(CH₃CN)₄BF₄—surprisingly, the acetylation reaction was very sluggish, proceeding to completion in 6 h and affording the phenyl acetate in a 92% yield.

These results may suggest the crucial role of the triflate counter ion in the observed catalyzed acylation reactions and may also suggest the likelihood of an ancillary side reaction due to Bronsted catalysis.

3. Experimental Section

3.1. Materials and Methods

All other chemicals were obtained from commercial vendors and used without further purification.

All acylation reactions were performed in a dried and argon flushed round bottom flask. The reaction's progress was routinely monitored by analytical thin-layer chromatography (TLC) using a pre-coated silica gel glass plates. The products were identified and analyzed using IR, ¹H NMR, and ¹³C NMR. The ¹H NMR spectra were recorded on a Varian 600 MHz spectrometer (Agilent Technologies, Santa Clara, CA, USA.).

The ¹³C NMR spectra were recorded on a Varian 150 MHz spectrometer (Agilent Technologies, Santa Clara, CA, USA.) using CDCl₃ as reference solvent.

3.2. Typical Experimental Procedure for O-Acetylation of Alcohols with Acetic Anhydride

An oven-dried and argon flushed 10 mL round-bottom flask was charged with Phenol (47.1 mg, 0.50 mmol, 1.0 equiv.) and acetic anhydride (0.19 mL, 2.0 mmol, 4.0 equiv.). To this mixture,

tetrakis(acetonitrile)copper(I) triflate (1.9 mg, 0.005 mmol, 1 mol %) was added. The reaction mixture was stirred at room temperature and monitored by TLC. When the reaction was complete, the excess acetic anhydride was decomposed with saturated aqueous NaHCO₃ (2 mL) and stirred for 45 min. The resulting reaction mixture was directly introduced onto a short SiO₂ column and purified by flash column chromatography (6/1, hexanes/ethyl acetate) to afford the phenyl acetate as pale yellow oil.

3.3. Typical Experimental Procedure for O-Acylation of Alcohols with Isobutyric Anhydride

An oven-dried and argon flushed 10 mL round-bottom flask was charged with phenol (47.1 mg, 0.50 mmol, 1.0 equiv.) and isobutyric anhydride (0.3 mL, 2.0 mmol, 4.0 equiv.). To this mixture, tetrakis(acetonitrile)copper(I) triflate (1.9 mg, 0.005 mmol, 1 mol %) was added. The reaction mixture was stirred at room temperature and monitored by TLC. When the reaction was complete, methanol (3 mL) was added and heated at 50 °C for 3 h. The resulting reaction mixture was concentrated in vacuo and purified by flash column chromatography (7/1, hexanes/ethyl acetate) to afford the phenyl isobutyrate as a pale yellow oil.

4. Conclusions

In summary, a new, simple, and highly efficient method of masking hydroxyl group to the corresponding esters mediated by tetrakis(acetonitrile)copper(I) triflate has been developed. This acylation protocol is mild and versatile, and mostly proceeds at room temperature.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/1/33/s1, Spectra data and Table S1: Preliminary studies of Cu(CH₃CN)₄OTf catalyzed acetylation of phenol.

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Conflicts of Interest: The authors declare no conflict of interest.

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