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Highly Efficient Cobalt (II) Catalyzed O-Acylation of Alcohols and Phenols under Solvent-Free Conditions

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ABSTRACT

Solvent free, highly efficient method has been developed using ecofriendly, heterogeneous reusable cobalt chloride catalyst at ambient reaction conditions for the O-acylation of various alcohols and phenols with acetyl chloride in excellent yield in a short reaction time. The catalyst is recycled several times without loss of catalytic activity.

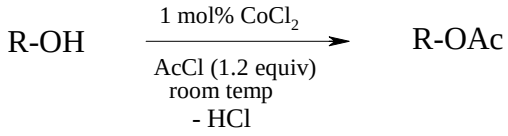
Keywords: Acetylation, Alcohol, Phenol, Acetyl Chloride, Cobalt (II) Chloride

1. Introduction

An esterification is a key and fundamental step to protect hydroxyl group during functional transformation in various organic synthesis [1-3]. However, protection and deprotection of hydroxyl functional group of alcohols and phenols being not only prime importance in pharmaceutical industries but also in the polymers, cosmetics, perfumes, plasticizers to achieve excellent yield to potential targeted synthetic compounds. Owing the importance of protection of hydroxyl functional group during the multisteps organic synthesis, the various methods for the protection of hydroxyl group of alcohols and phenols using varieties of reagent and catalysts such as $HgCl_2$ [4], Montmorillonite [5], TMS-Cl [6], $TaCl_5$-SiO_2 [7], $ZnCl_2$ [8], ZnO [9-10], Ru-catalyst [11], $Mg(ClO_4)$ [12], SmI_2 [13], $CeCl_3$ [14], perchlorates [15], P_2O_5/Al_2O_3 [16], $CoCl_2$ [17-18], $ZrCl_4$ [19], NH_2SO_3H [20], solid supported HBF_4-SiO_2 [21], lipase enzyme [22], $Al(OTf)_3$ [23], $In(OTf)_3$ [24], $Bi(OTf)_3$ [25], polymer supported $Gd(OTf)_3$ [26], $Ce(OTf)_3$ [27], $Ag(OTf)_3$ [28], molecular Iodine [29], nitro benzeneboronic acid [30], $NiCl_2$ [31], $La(NO_3).6H_2O$ [32], DCC [33], Co(II)salen-complex [34], Melamine trisulfonic acid (MTSA) [35], ionic liquid [36-39], $ZnAl_2O_4$ [40], have been reported, however, the most common acetylating reagents used are acetyl chloride, acetic acid, acetic anhydride or any other protic acid [41].

However, all the above methods are badly suffer from one/or other limitations and drawbacks such as drastic reaction conditions, long reaction time, high temperature, use of moisture sensitive, toxic, expensive reagents and catalysts. In addition these limitations, the catalysts are non-recoverable besides the formation of toxic side product and poor yield for the desired product in presence of organic solvent.

Therefore, considering all the above facts, still there is a need and demand to develop a solvent free, greener and an economical protocol and catalysts for protection of hydroxyl of alcohols and phenols by esterification. Therefore, herein we wish to report a solvent-free, a cheap, mild, rapid and efficient protocol for the O-acylation of alcohols and phenols with acetyl chloride over cobalt (II) chloride catalyst at room temperature (**Schemes 1**).



R= Ph, Allyl, Benzyl, Naphthyl, Aliphatic, etc.

Scheme 1. Cobalt (II) chloride catalyzed O-acylation of alcohols and phenols.

2. Experimental Section

All chemicals and reagents were procured from suppliers and used without further purification. The products were analyzed by a 5765 NUCON Gas Chromatograph with FID detector using stainless steel column 4 m length x 1/8 inch O.D. x 2 mm I.D., packed with 10% SE-30 on Chromosorb-W with mesh size 80-100 and also characterized using ^1H NMR, ^{13}C NMR spectra. The NMR spectrums of product were obtained using Bruker AC-200 MHz spectrometer with TMS as the internal stan-

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dard.

2.1 General Experimental Procedure for O-Acetylation of Alcohols and Phenols

The alcohol or phenol (5 mmol) in acetyl chloride (6 mmol) was taken in 50 ml round bottom flask. To this reaction mixture 1mol% cobalt (II) chloride catalyst was added and then mixture was stirred at room temperature under solvent free conditions. The influence of acylating agents was investigated using phenol, 4-methyl phenol and chloroethanol as substrate. The completion of the reactions was monitored by GC. After the completion of reaction, the mixture was diluted with ethyl acetate (25 ml) and the catalyst was recovered by filtration. The filtrate was washed with $NaHCO_3$ and then with water, dried over anhydrous Na_2SO_4. The dry filtrate was concentrated under vacuum to obtain the pure product.

3. Results and Discussion

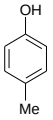
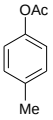
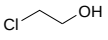
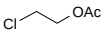
Acylation of phenol (5 mmol) was studied with acetyl chloride (6 mmol) in presence of 1 mol% cobalt (II) chloride catalyst under solvent free condition at room temperature to afford phenyl acetate in 99% yield in 20 seconds. However, the acetylation reaction of phenol was inefficient in absence of cobalt (II) chloride. After the successful acetylation of phenol with excellent yield to phenyl ester, the influence of acylating agents was invest tigated using phenol, 4-methyl phenol and chloroethanol as substrate and results are summarized in **Table 1**. The influence of the acylating agent's study (entries 1 - 3, **Table 1**) reveals that reactivity of acetyl chloride is ex tremely higher than that of acetic anhydride and acetic acid over the cobalt (II) chloride catalyst under solvent free conditions at room temperature.

The results on influence of acylating agents promoted us to evaluate the scope of this methodology for different types of primary, secondary, benzylic, allylic, cyclic alcohols and phenols using acetyl chloride as acylating agent (**Scheme 1**).

A number of substituted phenols and alcohols such as 4-tert-butyl phenol, 2- tert-butyl, 4-methyl phenol, p-cresol, o-cresol, m-cresol, 2-hydroxy benzaldehyde, 1-naphthol and 2-naphthol (entries 2 - 9, **Table 2**) and butanol; hexanol; heptanol; 1, 8-octandiol; chloro ethanol; Lauryl alcohol and 2-butanol (entries 1 - 7, **Table 3**), secondary alcohols (entries 8 - 9, **Table 3**), allylic alcohol (entry 10, **Table 3**) and benzylic alcohols (entry 11 - 12, **Table 3**) were acetylated respectively, in good to excellent yield without any difficulties.

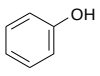
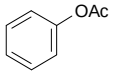
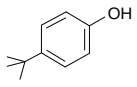
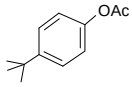
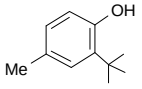
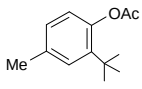
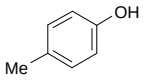
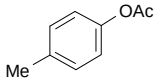
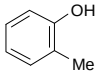
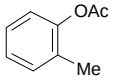
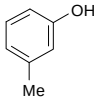
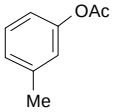
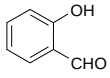
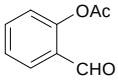
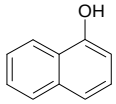
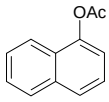
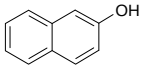
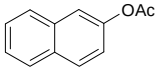
The results (**Tables 2 and 3**) on the acetylation of alco hols and phenols reveal that the good to excellent yield up to 99% was achieved in very short reaction time

Table 1. Influence of acylating agents on various substrate[a].

Entry	Substrate	Product	Time (s)	(%) Yield[b]		
				AcCl	Ac_2O	AcOH
1			20 3600	99 -	NR NR	NR NR
2			15 3600	99 -	35 39	NR NR
3			10 3600	99 -	67 99	NR 12

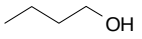
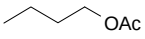
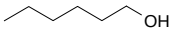
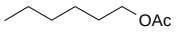
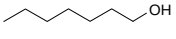
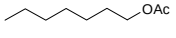
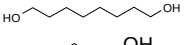
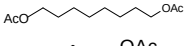
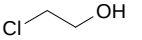
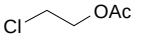
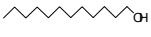
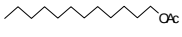
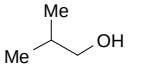
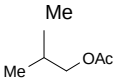
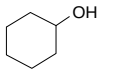
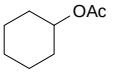
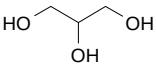
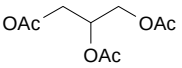
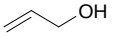
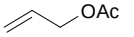
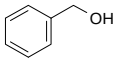
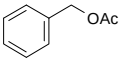
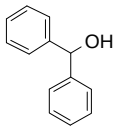
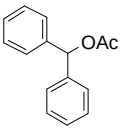
[a]Reaction conditions: The substrate (5 mmol), acetylating agent (6 mmol), 1 mol% $CoCl_2$, room temperature; [b]GC yield. NR: No Reaction.

Table 2. Cobalt (II) chloride catalyzed acetylation of phenols with acetyl chloridea.

Entry	Substrate (R)	Product	Time (s)	Yield[b] (%)
1			20	99
2			20	99
3			25	89
4			15	99
5			20	99
6			20	99
7			40	99
8			15	99
9			20	99

[a]Reaction conditions: The substrate (5 mmol), CH_3COCl (6 mmol/OH group), 1 mol% $CoCl_2$, room temperature; [b]GC yield; [c]without $CoCl_2$ catalyst.

Table 3. Cobalt (II) chloride catalyzed acetylation of alcohols with acetyl chloride[a].

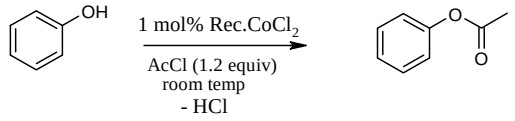
Entry	Substrate (R)	Product	Time (s)	Yield[b] (%)
1			10	95
2			10	99
3			15	98
4			15	99
5			10	99
6			15	99
7			10	98
8			10	99
9			35	92
10			10	82
11			50	75
12			35	98

[a]Reaction conditions: The substrate (5 mmol), CH_3COCl (6 mmol/OH group), 1mol % $CoCl_2$, room temperature; [b]GC yield.

(10 - 50 seconds). Further, the result indicates that the cobalt (II) chloride catalyst shows remarkably high catalytic activity and efficiency not only with primary alcohols and phenols but also with sterically hindered secondary, benzylic, allylic, cyclic alcohols and phenols under mild and solvent free reaction conditions at room temperature. The catalytic activity and/ or recyclability study of 1 mol% cobalt (II) chloride catalyst was performed for the acetylation of phenol (**Scheme 2**, **Table 4**).

The catalyst was recovered quantitatively four times by simple filtration of the reaction mixture and subsequently washed with ethyl acetate and water. The recovered cobalt (II) chloride catalyst was reused four times (Run 2-5, **Table 4**) for the acetylation of phenol with acetyl chloride to give the phenyl acetate in 98% - 99% yield, which is almost comparable with fresh catalyst (Run 1, **Table 4**). This result clearly shows that the recycled cobalt (II) chloride gives excellent yield without loss of catalytic activity.

As shown in the **Scheme 3,** the plausible reaction mechanism and/ or catalytic cycle for the acetylation of alcohols and phenols using acetyl chloride as acylating agents over the cobalt (II) chloride under the solvent free

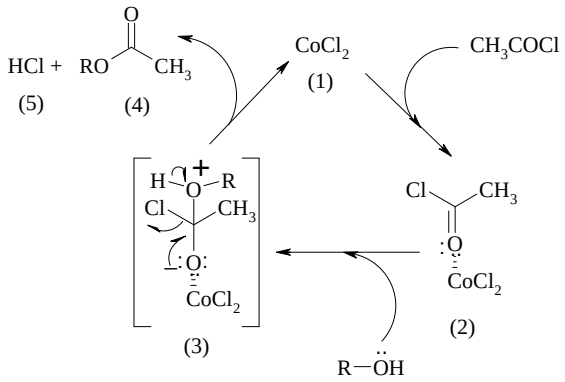


Scheme 2. Recyclability study of cobalt (II) chloride catalyst for acetylation of phenols with acetyl chloride.

Table 4. Recyclability study of cobalt (II) chloride for acetylation of phenol with acetyl chloride[a].

No. of Run	Time (s)	Yield (%)
Run 1 (Fresh catalyst)	20	99
Run 2	20	99
Run 3	25	98
Run 4	25	99
Run 5	30	99

[a]Reaction conditions: phenol (5 mmol) CH_3COCl (6 mmol) 1 mol% of $CoCl_2$ at room temperature Catalyst recovery = 97% ± 2%; [b]GC yield.



R= Ph, Allyl, Benzyl, Naphthyl, Aliphatic, etc.

Scheme 3. The proposed catalytic cycle for the acetylation reaction over $CoCl_2$ catalyst.

condition at room temperature is not clear so far, however, the results obtained in the present study shed some light on these aspects.

The carbonyl group of acetyl chloride is known to coordinating on Lewis acid sites of the $CoCl_2$ catalyst surface via intermediate (2) to activate itself being reactive electrophile. The activation of carbonyl group of acetyl chloride encourage the attack by the oxygen of alcohols and/or phenols as an nucleophile and subsequently stabilization intermediate (3) and release of leaving group followed by formation of the corresponding acetate (4) by the loss of hydrochloric acid (5).

4. Conclusions

In conclusion, cobalt (II) chloride is an efficient, versatile, ecofriendly, inexpensive, nontoxic, reusable heterogeneous and green catalyst for the acetylation of alcohols and phenols using acetyl chloride as acetylating reagent. The following features make this methodology attractive: 1)

its simplicity, clean, efficient, rapid and mild reactions conditions; 2) the protocol is very general and it works well with variety of alcohols and phenols affording good to excellent yields; 3) the reaction carried out at room temperature in absence of the organic solvent; 4) the relative reactivity of acylating agents over the cobalt (II) chloride catalyst were found to be higher in the order: acetyl chloride > acetic anhydride > acetic acid; 5) the recovered and reused catalyst without further purifica tions gave 98% - 99% yield without loss of catalytic activeity.

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