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# Copper perchlorate: Efficient acetylation catalyst under solvent free conditions

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#### **Abstract**

Acetylation of alcohols, phenols, amines, thiols and aldehydes is performed using acetic anhydride as acylating agent and  $M(ClO_4)_2 \cdot 6H_2O$  as catalyst where M is Mn, Co, Ni, Cu and Zn at room temperature under solvent free conditions. Transition metal perchlorates used here are found to be more efficient than the already reported metal triflates and s, p-block perchlorates. Substrates containing acid sensitive protecting groups are acylated successfully without any cleavage of the protection. Remarkably, less nucleophlic thiols (e.g. 2-mercaptobenzothiazole) are acylated with reasonable yields using transition metal perchlorates as catalyst whereas otherwise active acylation catalyst  $Mg(ClO_4)_2$  was found to be inefficient. © 2006 Elsevier B.V. All rights reserved.

Keywords: Acylations; Heteroatoms; Aldehydes; Transition metal perchlorates; Catalysis

#### 1. Introduction

Protection of aldehydes and heteroatoms such as alcohols, phenols, amines and thiols are primary important functional group transformations in organic synthesis usually achieved by using acetic anhydride [1,2]. Several methods are available to protect the heteroatoms [3–21] and aldehydes [22–34] by using various metal salts e.g. chlorides, triflates, perchlorates, etc. and supported catalysts. Acylation of heteroatoms under solvent and catalyst free conditions is conducted under reflux at 85 °C [2d]. However, the search of suitable catalysts for acylation that can be used under milder conditions remains as a continued field of research.

The limitations of certain acylation protocols are recognized as follows: expensive catalysts (e.g. triflates) [8,9,22,24], environmentally harmful organic solvents (e.g. CH<sub>2</sub>Cl<sub>2</sub> [8,10,23], CH<sub>3</sub>CN [25], CH<sub>3</sub>NO<sub>2</sub> [22]), longer reaction time and incomplete reaction [3,4]. In addition the metal triflates may involve competitive side reactions (e.g. dehydration and rearrangement) with acid-sensitive substrates due to large negative Ho value of TfOH [35]. Since perchloric acid is weaker than triflic acid [36] the use of metal perchlorates should reduce the side reactions

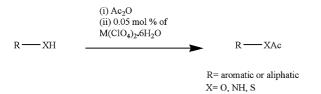
[36]. Among the metal perchlorates, LiClO<sub>4</sub> [11], Mg(ClO<sub>4</sub>)<sub>2</sub> [12], BiOClO<sub>4</sub> [13], and Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O [14] were used for protection of heteroatoms. To the best of our knowledge, there is no report available for the protection of aldehydes utilizing any kind of perchlorates. Furthermore transition metal perchlorates are not exploited for heteroatom acylation.

In this article we report use of various salts of general formula M(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O where M is Mn, Co, Ni, Cu and Zn as efficient catalysts for acetylation of heteroatoms (Scheme 1) and diacetylation of aldehydes (Scheme 2) under solvent free conditions at room temperature. The catalysts are found to be more efficient compared to the other metal perchlorates and triflates reported earlier and the comparison is shown in this work.

#### 2. Results and discussion

In our preliminary experiments, we have used benzyl alcohol and benzaldehyde as model substrates with acetic anhydride as acetylating agent and  $Cu(ClO_4)_2 \cdot 6H_2O$  as catalyst. In the case of acetylation of benzyl alcohol, 10 mmol of benzyl alcohol was added to 1 equiv. of acetic anhydride followed by 0.05 mol% of  $Cu(ClO_4)_2 \cdot 6H_2O$  and the mixture was stirred at room temperature. The desired reaction finished within 5 min giving quantitative yield of benzyl acetate with 99% purity as measured by GC. For acetylation of benzaldehyde similar procedure was adopted with 2 equiv. of acetic anhydride. The desired reaction finished

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Scheme 1. Acetylation of hetero atoms using  $M(ClO_4)_2 \cdot 6H_2O$  as catalyst, where M is Mn, Co, Ni, Cu and Zn.

$$\begin{array}{c} \text{(i) } Ac_2O \\ \text{(ii) } 0.05 \text{ mol } \% \text{ of} \\ M(ClO_4)_2.6H_2O \\ \end{array} \qquad \begin{array}{c} \text{R} \\ \text{OAc} \\ \text{H} \\ \end{array}$$

Scheme 2. Diacetylation of aldehydes using  $M(ClO_4)_2$ - $6H_2O$  as catalyst, where M is Mn, Co, Ni, Cu and Zn.

with in a minute giving quantitative yield of benzylidene diacetate with 99% purity as measured by GC.

To check the effect of solvent, amount of catalyst and amount of acylating agent on the reaction, the acetylation of benzyl alcohol was carried out in different conditions using Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O as catalyst. Solvents such as AcOH, CH<sub>2</sub>Cl<sub>2</sub>, THF, CH<sub>3</sub>CN, and Et<sub>2</sub>O were used for the reaction and compared with the result obtained under solvent free conditions (Table 1). The amounts of catalyst and acylating agent under solvent free conditions were also performed (Table 1). Blank experiments were performed in the absence of catalyst at room temperature and compared with earlier data [2d] on acetylation in the absence of catalyst at 85 °C (Table 2). We carried out diacetylation of benzaldehyde in the absence of catalysts at room temperature and 85 °C in this work since such data is not available in literature. It was observed that, under solvent free conditions or using AcOH as solvent the reaction was faster. There was no appreciable effect of the amount of catalyst (range: 0.01–0.1 mol%) on reaction time. However, with increased amount of the acylat-

Table 1
Room temperature acetylation of benzyl alcohol (10 mmol) in various solvents and solvent free conditions using the Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O catalyst

Catalyst (mol %)	Solvent (ml)	Ac <sub>2</sub> O (equiv.)	Time	Yield (%) <sup>a</sup>
	AcOH (3)	1	15 min	93
	$CH_2Cl_2$ (3)	1	5 h	Trace
0.05	THF (3)	1	5 h	Trace
0.05	CH <sub>3</sub> CN (3)	1	5 h	23
	$Et_2O(3)$	1	5 h	53
	_	1	5 min	97
0.01	_	1	8 min	97
0.01	_	2	5 min	97
0.07	_	1	5 min	97
0.05	_	2	3 min	97
0.4	_	1	5 min	97
0.1	_	2	3 min	97
0.7	_	1	5 min	97
0.5	-	2	2 min	97

a Isolated yield.

Table 2
Acetylation of heteroatoms and aldehydes in the presence and absence of the catalyst<sup>a</sup>

Substrate	Catalyst <sup>b</sup> (mol %)	Ac <sub>2</sub> O (equiv.)	Time	Yield (%) <sup>c</sup>
	_	1	24 h	28
PhCH <sub>2</sub> OH	_	1.2	2 h	95 <sup>d</sup>
	0.05	1	5 min	97
	_	1	24 h	32
PhOH	_	1.2	1.5 h	80 <sup>d</sup>
	0.05	1	1 min	97
	_	1	24 h	41
PhSH	_	1.2	1.5 h	82 <sup>d</sup>
	0.05	1	1 min	97
	_	1	2.5 h	91
PhNH <sub>2</sub>	_	1.2	0.5 h	93 <sup>d</sup>
	0.05	1	1 min	97
	_	2	24 h	8
PhCHO	_	2	24 h	39e
	0.05	2	1 min	97

<sup>&</sup>lt;sup>a</sup> All the reaction were carried out under solvent free condition at room temperature unless otherwise mentioned.

ing agent i.e. acetic anhydride, the reactions proceeded slightly faster. In the absence of catalyst at room temperature the reactions are unfinished even after longer time like 24 h. Refluxing at 85 °C drives the reaction faster but requires about 2 h for heteroatoms [2d]. For benzaldehyde refluxing is not very effective in the absence of catalyst even after a period of 24 h. To check the catalyst efficiency in general (conditions: at room temperature in the presence of catalyst), after reaction is complete a fresh batch of substrate and acetic anhydride was added to the same flask, which showed a similar reactivity again. Further, the process was able to be repeated several times.

Learning from the results above mentioned we decided on the ideal conditions of acylation reaction as (i) solvent free, (ii) room temperature, (iii) 0.05 mol% of catalyst. Thus, substrates of different natures such as various kinds of alcohols, phenols, amines, thiols and aldehydes are examined under these conditions and the result is summarized in Tables 3–6. The variety of catalysts employed for all the substrates are the perchlorates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).

Summary of the catalyzed acetylation of alcohols by the catalysts is provided in Table 3. Among the aliphatic alcohols, primary (entries 1-3), allylic (entries 4 and 5), secondary (entries 7 and 8), *tert*-propargylic (entry 6) and benzylic alcohols (entries 9-16) are used as substrates and acetylated successfully. The reactions were carried out at  $15-20\,^{\circ}\mathrm{C}$  for allylic and propargylic alcohols (entries 4-6) and isopropylidene and TBS protected alcohols (entries 3 and 10). All the five perchlorates used except  $\mathrm{Mn}(\mathrm{ClO}_4)_2 \cdot 6\mathrm{H}_2\mathrm{O}$  (for entries 3 and 7) are efficient.

Substrates used for acetylation of phenolic compounds are provided in Table 4. All the perchlorates have proved to be successful catalysts for all the phenolic compounds used (entries

<sup>&</sup>lt;sup>b</sup> Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O as catalyst.

<sup>&</sup>lt;sup>c</sup> Isolated yield.

 $<sup>^{\</sup>rm d}$  The reaction was carried out at 85  $^{\circ}$ C in the absence of catalyst and solvent free conditions and reported [2d].

<sup>&</sup>lt;sup>e</sup> The reaction was carried out at 85 °C.

Table 3 Acetylation of various alcohols catalysed by transition metal perchlorates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) $^a$ 

Entry	Substrate	Time (min)	Yieldb	
	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH			
1		10–15	97	
	OCH <sub>2</sub> CH <sub>2</sub> OH			
2		5–10	97	
	$0 \longrightarrow 0$		a=a d	
3	<sup>0</sup>	20–30	97 <sup>c,d</sup>	
4	CH <sub>2</sub> OH	10–15	97°	
	Me			
5	ОН	10–15	97 <sup>c</sup>	
	Me Me			
6	$\equiv \stackrel{\mathrm{OH}}{\smile}$	20–30	97 <sup>c</sup>	
	Me			
7	ОН	10–15	97 <sup>d</sup>	
	Me Me			
0	OH 人	10–15	97	
8		10–13	91	
	CH <sub>2</sub> OH ↓			
9		5–8	97	
	CH <sub>2</sub> OH ↓			
10		2–5	97 <sup>c</sup>	
	OTBS			
11	CH <sub>2</sub> OH NO <sub>2</sub>	5–10	97	
	CH OH			
	CH₂OH			
12		2–5	97	
	Br CH <sub>2</sub> OH			
13		2–5	97	
	ÓН			
14		5–10	97	
	ОН			
15		5–10	97	
	OH 1 Ph			
16	Fil	5–8	97	
	<b>V</b> 0			

 $<sup>^{\</sup>rm a}$  Reaction conditions: 10 mmol substrate/1 equiv. Ac<sub>2</sub>O/0.05 mol% catalyst/rt.

Table 4 Acetylation of various phenols catalysed by transition metal perchlorates of Mn(II), Co(II), Ni(II), Cu(II) and  $Zn(II)^a$ 

Entry	Substrate	Time (min)	Yield <sup>b</sup>
17	OH	1–5	97
18	OH CH <sub>3</sub>	2–5	97
19	Me OH Me	10–15	97°
20	OH Me Me Me	10–15	97 <sup>c</sup>
21	$\bigvee_{NO_2}^{OH}$	2–5	97 <sup>c</sup>
22	ОН	5–10	97
23	ОН	5–10	97
24	OH N	5–6	97
25	OH	5–10	97
26	ОН	1–2	97 <sup>d</sup>
27	ОН	1–2	97 <sup>d</sup>
28	ОН	1–5	97 <sup>d</sup>

 $<sup>^{\</sup>rm a}$  Reaction conditions: 10 mmol of substrate/1 equiv. Ac<sub>2</sub>O/0.05 mol% catalyst/room temperature.

17–18 and 21–28) except entries 19 and 20. For the substrates 19 and 20 having ortho substituted alkyl groups, all catalysts except Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O are efficient. Different kinds of dihydroxy phenolic compound (entries 26–28) is acetylated quantitatively.

Results obtained from the acylation of amines (entries 29–37) and thiols (entry 38–44) are provided in Table 5. Various kinds of amine and thiol are acylated with all perclorates smoothly. However, for acetylation of thiazole deriva-

b Isolated yield in the case of catalyst with M=Cu other catalysts also gives comparable yields.

<sup>&</sup>lt;sup>c</sup> The reaction was carried out at 15–20 °C.

 $<sup>^</sup>d$  Mn(ClO\_4)2·6H\_2O is not effective for the substrate while other catalysts are efficient.

<sup>&</sup>lt;sup>b</sup> Isolated yield in the case of catalyst with M=Cu other catalysts also gives comparable yields.

 $<sup>^</sup>c\ Mn(ClO_4)_2\cdot 6H_2O$  is not effective for the substrate while other catalysts are efficient.

<sup>&</sup>lt;sup>d</sup> 2.5 equiv. Ac<sub>2</sub>O was used/product found as diacetate.

Table 5

Table 6 Acetylation of various amines and thiols catalyzed by transition metal perchlorates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)<sup>a</sup>

Entry	Substrate	Time (min)	Yieldb	
	$^{ m NH_2}$			
29		5	96	
	$NH_2$			
30		1	97	
	$NH_2$			
.1		1	07	
31	CH <sub>3</sub>	1	97	
	NH <sub>2</sub>			
32		1	95	
	Y Br NH <sub>2</sub>			
	NH <sub>2</sub>			
33		1	96	
	Ċl NH <sub>2</sub>			
34	OH CH	6–10	95c,d	
	$NH_2$			
35	O <sub>2</sub> N	10–15	90	
36	$NH_2$ $NO_2$	12–15	93	
	NH <sub>2</sub>			
37		1	97	
	SH			
38	Į.	10–15	97	
39	SH	1	98	
		-		
	SH			
40		1	96	
	$ m CH_3$ SH			
<b>4</b> 1		3	96	
•	OCH <sub>3</sub>	J	, ,	
12	SH	10.15	92 <sup>c,d</sup>	
12	ОН	10–15	920,4	
13	$\begin{bmatrix} S \\ \rightarrow SH \\ N \end{bmatrix}$	30	97 <sup>d,e</sup>	
14	$S \rightarrow SH$	60	47 <sup>d,e</sup>	
	N SII		7/	

lyst/room temperature.

Acetylation of various aldehydes catalysed by transition metal perchlorates of

Entry	Substrate	Time (min)	Yieldb
45	СНО	1	98
46	СНО	1	97
47	CHO Cl	2–5	97
48	CHO Br	2–5	95
49	CHO Me	1–5	96
50	CHO NO <sub>2</sub>	6–10	95
51	CHO NO <sub>2</sub>	5–10	97
52	CHO COCH <sub>3</sub>	10	93
53	СНО	1–2	97
54	CH=CH-CHO	15–25	97°
55	СН <sub>2</sub> СН <sub>2</sub> СНО	5–10	98
56	CHO	30	96 <sup>d</sup>
57	СНО	30	96 <sup>d</sup>
58	CHO OH	30	92 <sup>d</sup>

<sup>&</sup>lt;sup>b</sup> Isolated yield in the case of catalyst with M=Cu other catalysts also gives comparable yields.

<sup>&</sup>lt;sup>c</sup> Product found as diacetate.

 $<sup>^{\</sup>rm d}~2.5\,equiv.~Ac_2O$  was used.

 $<sup>^</sup>e\,\,\text{Mn}(\text{ClO}_4)_2\!\cdot\!6\text{H}_2\text{O}$  is not effective for the substrate while other catalysts are efficient.

Table 6 (Continued)

Entry	Substrate	Time (min)	Yield <sup>b</sup>
59	CHO OH	30-45	97°
60	COCH <sub>3</sub>	60	$0^{\mathrm{f}}$

 $<sup>^</sup>a$  Reaction conditions: 10 mmol of substrate/1 equiv. of Ac<sub>2</sub>O/0.05 mol% catalyst/room temperature.

- <sup>c</sup> Reaction was carried out at 15–20 °C.
- $^{\rm d}$  4 equiv. Ac<sub>2</sub>O was used/product isolated as triacetate.
- <sup>e</sup> 5 equiv. of Ac<sub>2</sub>O was used/ product isolated as tetraacetate.
- f Keto groups remain unchanged.

tives e.g. 2-mercaptothiazoline and 2-mercaptobenzothiazole (entries 43 and 44) the catalyst  $Mn(ClO_4)_2 \cdot 6H_2O$  is found unsuitable.

The results of the diacetylation of aldehyde are collected in Table 6. Benzaldehyde derivatives (entries 45–53 and 56–59), allylic (entry 54), and aliphatic (entry 55) aldehydes are acetylated successfully with all catalysts. Hydroxy benzaldehydes (entry 56–59) containing two types of acylatable group are completely acetylated to corresponding acetoxybenzylidene diacetates. Neither acetophenone (entry 60) nor ketonic substrates (entry 52) is acylated by any of these catalysts at the keto position. In all the cases noted in Tables 3–6 manganese perchlorates showed comparatively less activity than the perchlorates of Co(II), Ni(II), Cu(II) and Zn(II). The later four perchlorates show efficient and approximately equal activity in terms of time required for the reaction. However, in ortho substituted phenols where the substituent is an acylatable group (entry 26) or unsaturated groups (entries 22, 25 and 28) Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O is also equally efficient in catalyzing the acetylation.

From the summary of the results we emphasize the following points: transition metal perchlorates used here are found to be much more active than s, and p-block metal perchlorates [11–13], e.g. as seen in acetylation of heteroatoms (Fig. 1). Among the transition metal perchlorates manganese perchlorate is slightly less active than others. We have observed in this work and mentioned earlier (Table 2) that at room tempera-

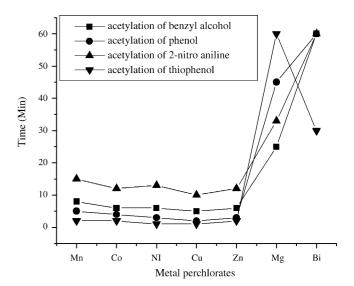


Fig. 1. Time required for complete acetylation of some heteroatoms using the perchlorates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The reported result is also plotted for comparison for the catalysts Mg(ClO<sub>4</sub>)<sub>2</sub> [12] and BiOClO<sub>4</sub> [13].

ture and in the absence of catalysts the substrate benzaldehyde is hardly acylated and at elevated temperature though the acylation takes place it is extremely sluggish and incomplete. In contrast, in the case of acetylation of aldehydes, metal perchlorates behave in a very efficient manner compared to heteroatom acylation. Comparison of gem-diacetylation of benzaldehyde by using metal perchlorates and reported [22–25] metal triflates are given in Table 7. Thus, the metal perchlorates may be considered more efficient and convenient as seen from the data collected in Table 7.

In the acylation of some synthetically important thiol compounds [37] such as 2-mercaptothiazoline and 2-mercaptobenzothiazole the efficiency is clearly remarkable when transition metal perchlorates used as catalyst in comparison with other metal perchlorates that were already used for the transformation. It is reported [12a] that  $Mg(ClO_4)_2$  cannot acylate 2-mercaptobenzothiazole even after 12 h. All perchlorates used in this study provide reasonable yield of acetylated product within 1 h (Scheme 3) except the Mn salt. The acetylated product of 2-mercaptobenzothiazole is a very important precursor to prepare  $\alpha$ -acylamino- $\beta$ -lactones, which are medicinally important (Scheme 4) [37].

Table 7
Formation of acylals of benzaldehyde by using transition metal perchlorates and metal triflates<sup>a</sup>

Catalyst (mol%)	Solvent	Temperature	Time	Yield (%) <sup>b</sup>	Ref.
$M(ClO_4)_2 \cdot 6H_2O^c (0.05)$	_	Room temperature	1–2 min	97	This work
LiOTf (20)	_	Room temperature	12 h	97	[24]
Bi(OTf) <sub>3</sub> ·4H <sub>2</sub> O (1.5)	_	-5 °C	20 min	87	[25]
$Bi(OTf)_3 \cdot 4H_2O(3)$	MeCN	Room temperature	40 min	91	[25]
$Cu(OTf)_2$ (2.5)	$CH_2Cl_2$	Room temperature	2 h	96	[23]
Sc(OTf) <sub>3</sub> (2)	$MeNO_2$	Room temperature	10 min	99	[22]

<sup>&</sup>lt;sup>a</sup> Reaction conditions: 0.05 mol% of catalyst/10 mmol of substrate/2 equiv. Ac<sub>2</sub>O.

<sup>&</sup>lt;sup>b</sup> Isolated yield in the case of catalyst with M=Cu other catalysts also gives comparable yields.

<sup>&</sup>lt;sup>b</sup> Isolated yield.

<sup>&</sup>lt;sup>c</sup> M = Mn, Co, Ni, Cu and Zn.

$$\begin{array}{c|c} S \\ S \\ N \end{array} = SH \\ \hline \begin{array}{c} Catalyst/Ac_2O/\ rt \\ \hline \end{array} \qquad \begin{array}{c} S \\ S \\ N \end{array} = SCOCH_3 \\ \hline \\ Mg(ClO_4)_2 & : \ No \ reaction \ (ref\ 12a) \\ \hline \\ M(ClO_4)_2.6H_2O & : \ 47\% \ (this \ work) \\ \hline \\ where \ M = Co, \ Ni, \ Cu, \ Zn \\ \hline \\ S \\ S \\ SCOCH_3 \\ \hline \\ Catalyst \\ \hline \\ Mg(ClO_4)_2 & : \ 65\% \ (ref\ 12a) \\ \hline \\ M(ClO_4)_2.6H_2O & : \ 96\% \ (this \ work) \\ \hline \\ where \ M = Co, \ Ni, \ Cu, \ Zn \\ \hline \end{array}$$

Scheme 3. Acetylation of synthetically important thiol compounds.

Scheme 4. Important use of S-benzothiazol-2-yl ethanethioate [37].

$$\begin{array}{c} \text{CH}_2\text{OH} \\ \text{OTBS} \end{array} \xrightarrow{M(\text{CIO}_4)_2.6\text{H}_2\text{O}/\text{Ac}_2\text{O}/\text{15-20 °C}} \begin{array}{c} \text{CH}_2\text{OAc} \\ \text{Where M=Mn,Co,Ni,Cu,Zn} \end{array}$$

Scheme 5. Acetylation of isopropylidene and TBS protected alcohols.

Protected alcohols such as isopropylidene glycerol and 4-(*tert*-butyldimethylsilyloxy)benzyl alcohol are successfully acylated to (2,2-dimethyl-1,3-dioxolan-4-yl)methyl acetate and 4-(*tert*-butyldimethylsilyloxy)benzyl acetate (Scheme 5) respectively without losing the protective groups, being also a point to note.

Hydroxybenzaldehydes are found to be completely converted to the corresponding acetoxy benzylidene diacetates (Scheme 6) within 30 min. This is in contrast to the fact that some of the reported catalysts provide lower yields also after longer time [26,34f] and that in some cases complex mixtures are formed [33] due to the activation of the ring by OH groups. Dihyroxybenzaldehydes also behaved in a similar manner and completely acetylated.

Scheme 6. Acetylation of hydroxy benzaldehydes at room temperature.

We suggest the role of metal perchlorates in catalysis should be the same as that of  $Cu(OTf)_2$  that is already proposed (Fig. 2) [10b].

Some of the advantages associated are noted here: solvent free and ambient reaction conditions, rapid reaction, quantitative yield, and no by-product formation from possible Fries rearrangement in the case of phenols. There is also a selectivity among the functional groups to get acylated if the reaction is carried out in a controlled manner. Acylation of substrates having weakly nucleophillic thiol groups like 2-mercaptothiazole is achieved in contrast to some other catalysts. Acylal formation from aldehydes is found to be very rapid and at the same time keto groups remain unchanged. Thus the transition metal perclorates are better for acetylation hederoatoms and aldehydes than other metal perclorates and metal triflates.

It may be mentioned that perchlorates are potentially explosive when heated in the presence of combustible substances at high temperature [38,39] and therefore care should be taken while handling perchlorates under such conditions. In the present work the requirement of only catalytic quantities of M(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and mild reaction conditions (room temperature) circumvented potential hazard if any associated with perchlorates and may make the methodology suitable for further use.

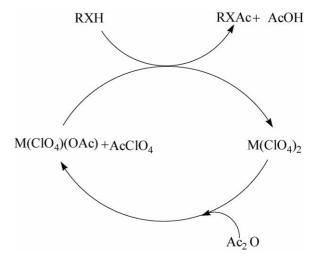


Fig. 2. Proposed mechanism for acetylation of heteroatoms.

## 3. Experimental

All metal perchlorates are purchased from Aldrich and used as such for reaction. All the acetylated products are characterized by recording their <sup>1</sup>H NMR, IR and melting points by using Bruker 400 MHz, Jasco FT/IR 660 plus and Toshnival-India melting point apparatus, respectively. The analytical data recorded are compared with reported data [40,41] of the compounds. For the acetylated products of the entries 44 and 56–59 we could not find analytical data in literature thus we present the data here in this work.

# 3.1. General procedure for acetylation of hetero atoms and aldehydes

An amount of 10 mmol of substrate was treated with required amount of acetic anhydride (for liquid substrate) or one to two-fold of acetic anhydride (for solid substrate) in the presence  $0.05\,\text{mol}\%$  of catalyst. The reaction mixture was stirred at room temperature under solvent free condition and progress of reaction was monitored by TLC. After reaction was complete, the reaction mixture was diluted with water and extracted with diethyl ether. The organic layer was separated and washed with saturated aqueous NaHCO3 and dried over anhydrous Na2SO4. Evaporation of ether gave the desired compound.

## 3.2. S-Benzothiazol-2-yl ethanethioate (product of entry 44)

Solid, m.p.:  $210\,^{\circ}$ C.  $^{1}$ H NMR ( $400\,\text{MHz}$ , CDCl $_3$ , TMS)— $\delta$  (ppm): 3.06 (s, 3H), 7.30–7.32 (m, 3H), 8.08–8.10 (m, 1H); IR (KBr): 1741 (CO), 1641 (CN) cm $^{-1}$ . C $_9$ H $_7$ NOS $_2$  (209.29): calcd. C 51.65, H 3.37, N 6.69; found C 51.61, H 3.30, N 6.63%.

# 3.3. 2-Acetoxy benzylidene diacetate (product of entry 56)

Solid, m.p.:105 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)— $\delta$  (ppm): 2.10 (s, 6H), 2.34 (s, 3H), 7.12 (d, J=7.8 Hz, 1H), 7.28–7.32 (m, 1H), 7.41–7.45 (m, 1H), 7.63 (d, J=7.8 Hz, 1H),7.89 (s, 1H). IR (KBr): 1742, 1745 cm<sup>-1</sup> (CO). C<sub>13</sub>H<sub>14</sub>O<sub>6</sub> (266.25): calcd. C 58.64, H 5.30; found C 58.58, H 5.28 %.

# 3.4. 3-Acetoxy benzylidene diacetate (product of entry 57)

Solid, m.p.:  $76 \,^{\circ}$ C.  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>, TMS)— $\delta$  (ppm): 2.12 (s, 6H), 2.31 (s, 3H), 7.14 (d, 1H), 7.39–7.41 (m, 3H), 7.67 (s, 1H). IR(KBr): 1741, 1745 cm<sup>-1</sup> (CO). C<sub>13</sub>H<sub>14</sub>O<sub>6</sub> (266.25): calcd. C 58.64, H 5.30; found C 58.55, H 5.29%.

#### 3.5. 4-Acetoxy benzylidene diacetate (product of entry 58)

Solid, m.p.: 95 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)— $\delta$  (ppm): 2.12 (s, 6H), 2.30 (s, 3H) 7.13 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.67 (s,1H). IR(KBr): 1740, 1746 cm<sup>-1</sup> (CO). C<sub>13</sub>H<sub>14</sub>O<sub>6</sub> (266.25): calcd. C 58.64, H 5.30; found C 58.61, H 5.27%.

3.6. 2,3 Diacetoxy benzylidene diacetate (product of entry 59)

Solid, m.p.:  $105\,^{\circ}$ C.  $^{1}$ H NMR ( $400\,\text{MHz}$ , CDCl<sub>3</sub>, TMS)— $\delta$  (ppm): 2.05 (s, 6H), 2.39 (s, 3H), 2.44 (s, 3H), 7.69 (s, 1H), 7.90-7.95 (m, 3H). IR(KBr): 1740,  $1747\,\text{cm}^{-1}$  (CO).  $C_{15}H_{16}O_{8}$  (324.28) calcd C, 55.56; H, 4.97; found C, 55.53; H,  $4.92\,\%$ .

#### 4. Conclusions

In conclusion we have demonstrated the use of transition metal perchlorates as efficient catalyst for acetylation of alcohols, phenols, amines, thiols and aldehydes at room temperature under solvent free conditions. The significant features of this method include ease of operation, high efficiency and mild conditions, which provide its possible utility in organic synthesis.

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