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Manganese-mediated acetylation of alcohols, phenols, thiols, and amines utilizing acetic anhydride

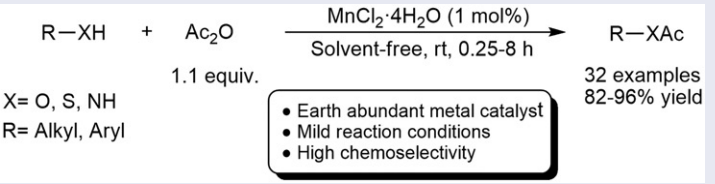
Isha Jain, Ramandeep Sharma, and Payal Malik

[1]Department of Chemistry, Sant Longowal Institute of Engineering and Technology, Longowal, India

ABSTRACT

Manganese(II) chloride-catalyzed acetylation of alcohols, phenols thiols and amines with acetic anhydride is reported. This method is environment-friendly and economically viable as it involves inexpensive, relatively benign catalyst, mild reaction condition, and simple workup. Acetylation is performed under the solvent-free condition at ambient temperature and acetylated products obtained in good to excellent yields. Primary, secondary heterocyclic amines, and phenols with various functional groups are smoothly acetylated in good yields. This method exhibits exquisite chemoselectivity, the amino group is preferentially acetylated in the presence of a hydroxyl/thiol group.

GRAPHICAL ABSTRACT



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KEYWORDS
Acetylation; acetic anhydride; manganese(II) chloride; solvent-free; chemoselectivity

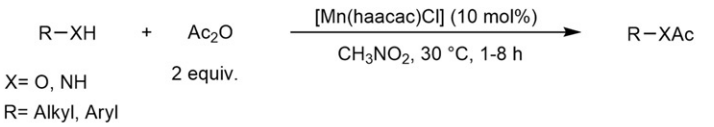
Introduction

Functional group protection is the most fundamental strategy for the synthesis of polyfunctional molecules.[1] Acetylation is a versatile method for masking of hydroxyl, sulfhydryl and amine groups.[2] Acetic anhydride is most commonly used acetylating agent.[3] Triethylamine, pyridine and 4-dimethylaminopyridine (DMAP) are employed as base catalysts for the acetylation of alcohols, phenols, and amines.[4] Various metal chlorides,[5] perchlorates,[6] triflates[7] and nitrates[8] have been used as active catalysts for acetylation. Though metal triflates and perchlorates demonstrated high catalytic efficiency for the acetylation reactions but a few limitations are associated with these methods, such as handling of hazardous perchlorates, the high price of metal triflates and some triflates required dry reaction conditions.[9]

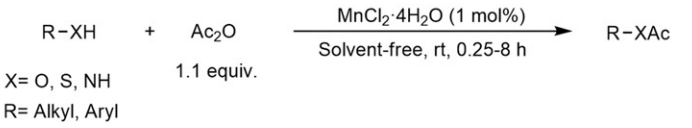
CONTACT Payal Malik msg.payal@gmail.com Department of Chemistry, Sant Longowal Institute of Engineering and Technology, Longowal 148106, India.

Supplemental data for this article is available online at on the publisher's website.

a) Pervious work: (bis(2-hydroxyanil)acetylacetonato)manganese(III)chloride catalyzed acetylation



b) This work: $MnCl_2{\cdot}4H_2O$ catalyzed acetylation



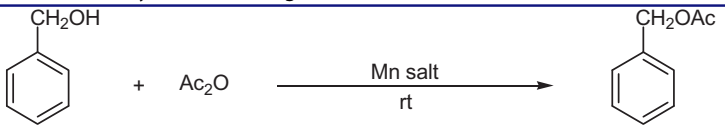
Scheme 1. Synthetic strategies for acetylation reactions.

Although the past two decades have witnessed remarkable advances in protection and deprotection chemistry,[10] from sustainability viewpoint still, there is a need for an economical, mild, and eco-friendly protocol for acetylation. In this regard, the third most abundant biocompatible transition metal in the Earth's crust, manganese (Mn) is a very attractive metal component for the development of cost-effective benign catalytic processes.[11] Recently, Mn salts are considered as an alternative to iron salts which resulted in an upsurge in Mn-chemistry.[12] $Mn(CH_3COO)_3$ and Mn(III) complexes are used as catalysts for acetylation of alcohols and amines (Scheme 1a).[13] However, high temperature, use of solvent, elaborated ligands and excess of Ac_2O make these methods less suitable. Herein, we describe a mild and simple protocol for acetylation of alcohols, phenols, thiols and amines using acetic anhydride as an acetylating agent in presence of readily available, moisture stable $MnCl_2{\cdot}4H_2O$ as catalyst under the solvent-free condition at ambient temperature (Scheme 1b).

Results and discussion

In initial attempts, acetylation of alcohol was carried out using benzyl alcohol (1 equiv.) as a model substrate with acetic anhydride (1.1 equiv.), in the presence of various Mn salts, as a catalyst at room temperature under solvent-free condition (Table 1). The catalytic efficiency of $MnBr_2$, $MnCl_2{\cdot}4H_2O$, and MnO_2 was tested for acetylation reaction, $MnCl_2{\cdot}4H_2O$ provided best results, 96% benzyl acetate was obtained within 1 h, in case of $MnBr_2$ and MnO_2, moderate yields were achieved. Moreover, in the absence of $MnCl_2{\cdot}4H_2O$, the reaction was sluggish and only 15% product was obtained after 24 h (Table 1, entry 6). Catalyst loading was optimized using a different amount of $MnCl_2{\cdot}4H_2O$, the reaction was slowed down when 0.5 mol% catalyst was used, whereas the increased catalyst ratio i.e. 1.5 mol% does not show a considerable effect on reaction time and product yield (Table 1, entries 4 and 5). The stoichiometric ratio between the reactants is very important from a green chemistry viewpoint. To minimize waste of reagents and make the purification process simpler we performed reaction using an equimolar amount of benzyl alcohol and acetic anhydride under the same conditions, desired product yield was reduced to 85%. To observe the solvent effect in this process,

Table 1. Acetylation of benzyl alcohol using different salts under solvent/solvent-free conditions[a].



Entry	Mn salt (mol%)	Time (h)	Solvent	Yield (%)[b]
1	$MnBr_2$ (1)	3.5	-	71
2	MnO_2 (1)	2	-	55
3	$MnCl_2{\cdot}4H_2O$ (1)	1	-	96
4	$MnCl_2{\cdot}4H_2O$ (0.5)	1	-	40
5	$MnCl_2{\cdot}4H_2O$ (1.5)	1	-	96
6	-	24	-	15
7	$MnCl_2{\cdot}4H_2O$ (1)	2	EtOAc	67
8	$MnCl_2{\cdot}4H_2O$ (1)	2	Et_2O	53
9	$MnCl_2{\cdot}4H_2O$ (1)	2	THF	78

[a]Reaction conditions: Alcohol (1 equiv.), acetic anhydride (1.1 equiv.), and Mn salt at 25 °C; [b]Isolated yield.

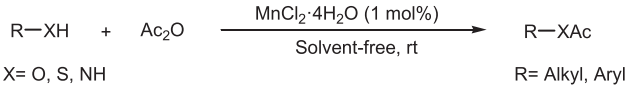
the acetylation was subsequently carried out in several solvents (e.g., EtOAc, Et_2O, and THF), and the results were compared with the solvent-free condition. It was found that the presence of solvent does not improve the product yields or reaction time.

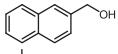
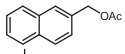
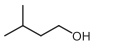
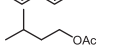
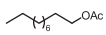
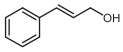
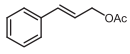
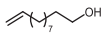
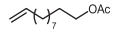
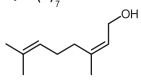
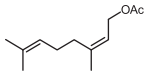
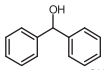
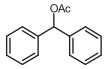
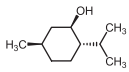
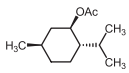
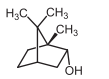
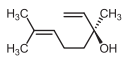
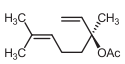
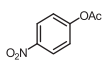
After optimization of the reaction conditions, various primary, secondary, tertiary and benzylic alcohols were subjected to acetylation and corresponding acetate derivatives were obtained in good to excellent yields (Table 2). Electron withdrawing groups like $-NO_2$ and –Cl retard the rate of acetylation reaction. Acetylation is relatively slow in case of long-chain aliphatic alcohols as compared to benzylic alcohols (Table 2, entries 1, 4, and 5). It was observed that acid-labile furfuryl alcohol provided better yields in THF (donor solvent), under solvent-free condition some complex by-product was also obtained along with the expected product (Table 2, entry 7). Acid-sensitive, chiral secondary and tertiary alcohols were successfully acetylated in high yields without any side reactions (Table 2, entries 8–17). Particularly, (−)-menthol, (−)-borneol and (−)-linalool retained their stereochemical configurations during the acetylation reaction, no racemization or epimerization was observed.

In addition, to extend the substrate scope this strategy was used for acetylation of various phenols, thiophenols and primary, secondary heterocyclic amines and corresponding acetate derivatives were obtained in good to excellent yields (Table 2, entries 18–32). No fries rearrangement was observed in the case of phenols. Acetylation reaction of aliphatic thiol was slow as compared to aromatic thiols (entries 27 vs. 25 and 26). Primary amines acetylated faster than the secondary amines. Notably, this method is highly chemoselective, 2-aminophenol and 2-aminothiophenol gave corresponding acetamides in excellent yields keeping the –OH and –SH functionalities unaltered (Table 2, entries 22 and 23). We performed an intermolecular competitive acetylation reaction, an equimolar mixture of aniline and phenol/thiophenol, was reacted with 1.1 equiv. of acetic anhydride in presence of $MnCl_2{\cdot}4H_2O$, aniline was acetylated selectively leaving the phenol/thiophenol unreacted. These excellent selectivities would make this strategy attractive for protecting group chemistry.

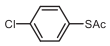
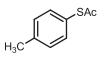
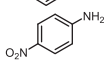
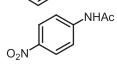
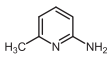
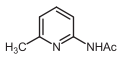
To gain insights into the mechanism of acetylation reaction, controlled experiments were performed. It has been observed that $MnCl_2$ catalyzed coupling reactions proceed through the SET mechanism.[11] Having that in mind, we carried out a radical

Table 2. Acetylation of alcohols, phenols, thiols, and amines[a].



Entry	Substrate	Product	Time (h)[b]	Yield (%)[c]
1			1	96
2			3	82
3			3.5	90
4			2	91
5			4	90
6			5.5	88
7*			5.5	90
8			4.5	89
9			4	91
10			4	90
11			3	88
12			4.5	90
13			5	92
14			4	90
15			5	89
16			6	90
17			3.5	87
18			3	88
19			4.5	82
20			4	83
21			4	90
22			0.5	92

(*continued*)

23			0.25	90
24			2.5	94
25			5	89
26			5.5	90
27			8	87
28			0.75	92
29			1.25	89
30	$(CH_3CH_2)_2NH$	$(CH_3CH_2)_2NH$	4.5	86
31			4	89
32			2.5	92

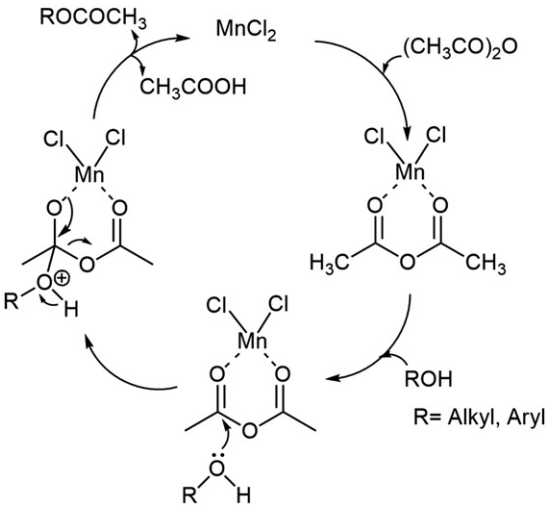
[a]Reaction conditions: Alcohol (1 equiv.), acetic anhydride (1.1 equiv.), and 1 mol% $MnCl_2{\cdot}4H_2O$ at 25 °C;
[b]Monitored using TLC until the alcohol/phenol/amine was consumed; [c]Isolated yield; *Reaction was performed in THF.

inhibition experiment by reacting benzyl alcohol with acetic anhydride in the presence of $MnCl_2{\cdot}4H_2O$ and 1 equiv. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a free radical quencher, 60% benzyl acetate was obtained after 1 h. The results ruled out the possibility of nonionic pathway.[5b]

In another controlled experiment, $MnCl_2{\cdot}4H_2O$ was reacted with acetic anhydride at room temperature and the reaction was monitored by NMR spectroscopy. ^{13}C NMR measurements of the reaction mixture (suspension) revealed that a small broad signal appears at δ 168 ppm along with acetic anhydride signal (δ 163 ppm). The change in chemical shift and broadening of signal suggest that the catalyst is coordinated with acetic anhydride, after addition of benzyl alcohol the signal was disappeared. There was no evidence for the formation of acetyl chloride. In addition, a broad peak at δ 11.5 ppm in the ^1H NMR spectrum of the reaction mixture indicates the formation of AcOH (all observed signals were broad due to the presence of Mn). On the basis of NMR observations, we proposed acetylation mechanism depicted in Scheme 2.

Conclusions

In summary, we have demonstrated that $MnCl_2{\cdot}4H_2O$ is an efficient catalyst for acetylation of alcohols, phenols, thiols, and amines under mild reaction conditions. All the acetate derivatives were isolated in high yields. Main features of this process are the use of stable, low cost, benign catalyst and the limited amount of acetic anhydride (1.1 equiv.), which makes the catalytic system more practical and environmentally viable. This method shows a broad substrate scope and excellent chemoselectivity without any ligand support.



Scheme 2. Proposed mechanism for $MnCl_2{\cdot}4H_2O$ catalyzed acetylation of alcohol. H_2O molecules are omitted for simplification.

General procedure for acetylation

To a stirred mixture of alcohol/phenol/thiohenol/amine (1 mmol) and acetic anhydride (1.1 mmol), 0.01 mmol of $MnCl_2{\cdot}4H_2O$ was added at room temperature. The reaction mixture was stirred until alcohol/phenol/thiohenol/amine was consumed, the progress of the reaction was monitored by TLC. The reaction mixture was quenched with saturated aq. $NaHCO_3$ and extracted with ethyl acetate (10 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was passed through a small pad of silica gel (eluent: hexane: ethyl acetate) to obtain pure acetates (acetamides were precipitated out/crystallized direct from the reaction mixture) and characterized by ^1H NMR and IR spectroscopy. The data was found to be in accord with previously reported acetates.

Characterization data and ^1H NMR spectra can be found via the "Supplementary Content" section of this article's webpage.

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ORCID

Payal Malik http://orcid.org/0000-0001-6764-209X

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