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# Manganese(III) bis(2-hydroxyanil)acetylacetonato complex as effective catalyst for acylation of alcohols, amines and phenols with acetic anhydride

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**Abstract**

Acylation of alcohols, amines and phenols with acetic anhydride in an efficient manner using [bis(2-hydroxyanil)acetylacetonato]manganese(III)chloride, [Mn(haacac)Cl], as a catalyst. Using this method acylation of a primary $NH_2$ group in the presence of secondary NH and primary OH have been achieved with high selectivity.


*Keywords:* Acylation; Mn(III); Schiff-base; Alcohol; Acetic Anhydride; Phenol; Amine

## 1. Introduction

The acylation of alcohols, phenols and amines is one of the most frequently used transformations in organic synthesis, as it provides an efficient and inexpensive means for protecting hydroxy and amino groups in a multistep synthetic process [1]. There are a variety of procedures for acylation of functional groups, the acylation of alcohols and amines is routinely carried out using acid anhydrides or acyl chlorides in the presence of tertiary amines such as $NEt_3$ and $C_5H_5N$ [2]. 4-(Dimethylamino)pyridine and 4-pyrrolidinopyridine are known to catalyse this reaction and to increase the rate of acylation [3]. Recently, Vedejs and co-workers reported tributylphosphine to be a similar catalyst for the acylation of alcohols [4]. In addition to the above catalysts, toluene-*p*-sulfonicacid [5], zinc chloride [6], cobalt chloride [7], scandium trifluoromethanesulfonate [8], tantal pentachloride [9], copper(II) triflate [10], $Me_3SiOTF$ [11], scandium triflate [8,12], indium(III) triflate [13], bismuth(III) triflate [14], lithium perchlorate [15], yttria-zirconica based Lewis acid [16], indium triiodide [17], montmorillonite K-10 and KSF [18], magnesium bromide [19], bismuth(III) salts [20], ferric perchlorate adsorbed on silica-gel [21], tin(IV) tyetraphenylporphyrin perchlorate [22], tin(IV) tetraphenylporphyrinato trifluoromethanesulfonato [23a], $ZrOCl_2{\cdot}8H_2O$ [23b], pillared clays [23c], ruthenium(III) chloride [23d], indium(III) chloride [23e], fluoroboric acid adsorbed on silica gel [23f], metallic Lewis acids [23g], iron(III) oxide-containing activated carbon [23h], solvent-free conditions at room temperature [23i], zeolite HSZ-360 [24] are also known to catalyse the acylation of alcohols and amines with acid anhydrides. Nevertheless, there is still a great demand for acid catalysts to generate esters under mild conditions and environmentally friendly processes.

The direct acylation of alcohols, amines and phenols with carboxylic acids, the Fisher esterification, can be performed by mineral acids or sulfonic acids where the only by-product is water, i.e. formally an atom economic process [25]. However, the reaction is reversible and required to excesses volume of either the alcohol or acid are required. Alternatively, Fisher esterifications can be driven for completion by azeotropic removal of water. However, the use of strong mineral acids leads to highly acidic waste streams posing an

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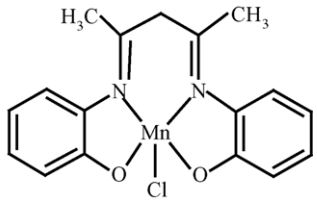


Scheme 1.

environmental problem for industrial processes. In order to circumvent the problem of equilibrium, typically acylation of alcohols is performed with activated acyl grouping, such as (mixed) acid anhydrides or acid chlorides with a stoichiometric quantity of amine base in the presence of basic catalysts [3,4,26]. Acylation process can also be performed by the action of Lewis acidic reagents in conjunction with carboxylic acids, but the Lewis acid is destroyed in the work-up procedure [27]. Similarity, Lewis acids are known to activate acid anhydrides for the acylation of alcohols [6], but the conversion is inherently wasteful since half of every acid anhydride molecule is lost as a carboxylic acid. Recently, the catalytic uses of metal triflates have been described for the acylation of alcohols with acid anhydrides, or with carboxylic acids. These disadvantages have negative impact on the environment. Manganese Schiff-base complexes are known to be active catalyst in the organic reactions [28]. In this work, we report acylation of alcohols, phenols and amines in excellent yields using acetic anhydride as acylating agent catalyzed by bis(2-hydroxyanil)acetylacetonatomanganese(III) chloride; [Mn(haacac)Cl] (Scheme 1).

## 2. Experimental

### 2.1. Preparation of Schiff-base ligand [28b]

2-Aminophenol (2.18 g, 0.02 mol) was dissolved in 75 ml ethanol, and a solution of acetylacetone (1.0 g, 0.01 mol) in 25 ml ethanol was added to it. The mixture was refluxed on a water bath for 8 h. After reducting the volume of the solution to ca. 50 ml, the flask was kept at ambient temperature for 4 h. On cooling the white–yellow crystalline Schiff base ligand was collected by filtration, washed with ethanol twice ($2 \times 20$ ml) and dried. Finally, the ligand was recrystallized from ethanol to give pure crystals, yield 84%. Anal. calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.12; H, 6.56; N, 10.06%. The $^1$H NMR spectrum of the tetradentate Schiff-base in chloroform shows the following signals: $C_6H_5$ multiplet at 6–9 $\delta$ range, $-CH_3$ at 1.90 $\delta$, $-CH_2$ at 2.27 $\delta$ and OH at 5.27 $\delta$.

### 2.2. Preparation of [bis(2-hydroxyanil)acetylacetonato]manganese(III)chloride

[Bis(2-hydroxyanil)acetylacetonato]manganese(III)chloride was prepared by following Jacobsen's procedure [29]. The Mn(III) haacac complex was prepared from 2.45 g (10 mmol) of $Mn(OAc)_2.4H_2O$ was added to 2.82 g (10 mmol) of $H_2$haacac ligand dissolved in ethanol (75 ml) and refluxed under air for 4 h at 80 °C. 1.27 g (30 mmol) of LiCl was added to the above mixture, refluxed for a further period of 3 h and cooled in ice. The brown [Mn(haacac)Cl] complex was filtered, washed with ethanol, ice-cold water and dried under vacuum for 8 h. Chemical analysis for $[C_{17}H_{16}N_2O_2MnCl]$: calcd. Mn, 14.83; C, 55.06; H, 4.35; N, 7.55; Cl, 9.57%. Found Mn, 14.71; C, 54.94; H, 4.27; N, 7.63; Cl, 9.48%. The complex was analyzed by UV and IR spectroscopy and spectrum is similar to that of Kochi's complex [30].

### 2.3. General procedure for acylation reactions

In a general round-bottom flask (25 ml) equipped with a magnetic stirrer, a solution of alcohol, phenol or amine (1 mmol) in acetic anhydride (two equivalents for each OH group of alcohol or phenol) and nitromethane (5 ml) was prepared. [Mn(haacac)Cl] (0.01 mmol) was added to this solution and the reaction mixture was stirred at 30 °C and reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was directly passed through a short column of silica-gel (hexane:ethyl acetate, 1:1, v/v) to remove the catalyst. The elute was evaporated under reduced pressure and the remaining residue was purified by silica-gel plate chromatography (eluted with $CCl_4$:$Et_2O$ = 9:1) to afford the corresponding ester without any elimination products.

## 3. Results and discussion

In a typical experimental procedure, the substrate (alcohol, phenol or amine) was heated at reflux in nitromethane in the presence of a catalytic amount of [bis(2-hydroxyanil)acetylacetonato manganese(III)chloride; [Mn(haacac)Cl]; for a certain period of time, reaction progress is monitored by TLC. The reaction mixture was directly passed through a short column of silica-gel. The elute was evaporated under reduced pressure and the remaining reside was purified by silica-gel plate chromatography. On the other hand, the reaction was conducted at room temperature to give lower yields, i.e. benzyl alcohol gave only 58% yield.

A wide range of alcohols, phenols and amines were subjected to acylation by this procedure. The results are reported in Table 1. It was found that primary alcohols (entries 1–12) and phenols (entries 13–19) underwent smooth acylation whereas secondary alcohols (entries 20, 21) remained inert even after prolonged treatment (24 h) under the present experimental conditions. On the other hand, a tertiary alcohol, suffered dehydration under these conditions (entry 27). The reaction conditions are not enough mild to induce any isomerisation of the double bond in allylic alcohols (entries 28, 29). In addition, a variety of other functional group like

Table 1
Acylation of alcohols using acetic anhydride catalysed by [Mn(haacac)Cl)] complex

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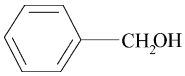
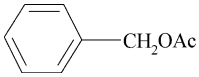
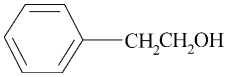
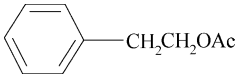
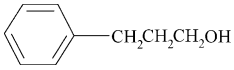
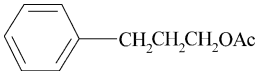
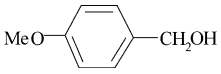
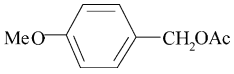
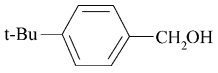
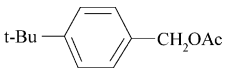
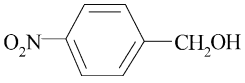
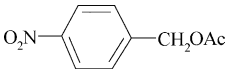
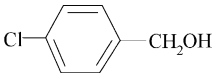
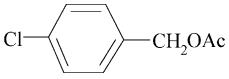
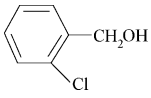
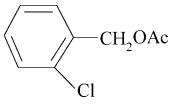
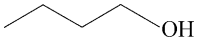
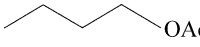
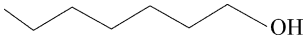
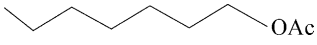
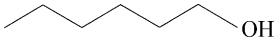
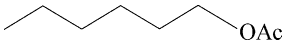
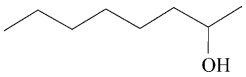
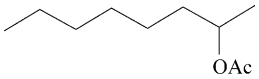
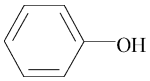
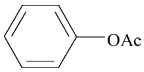
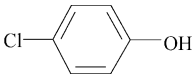
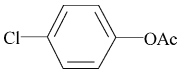
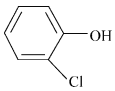
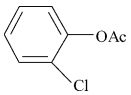
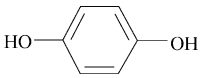
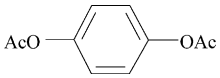
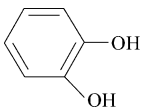
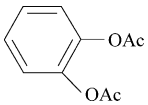
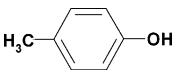
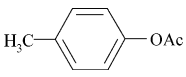
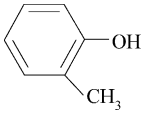
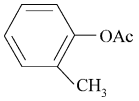
| 1 |  | 5 |  | 97 |
| 2 |  | 5 |  | 95 |
| 3 |  | 5 |  | 92 |
| 4 |  | 6 |  | 91 |
| 5 |  | 6 |  | 88 |
| 6 |  | 8 |  | 86 |
| 7 |  | 8 |  | 88 |
| 8 |  | 8 |  | 86 |
| 9 |  | 6 |  | 96 |
| 10 |  | 6 |  | 94 |
| 11 |  | 6 |  | 93 |
| 6 |  | 6 |  | 89 |
| 13 |  | 4 |  | 94 |
| 14 |  | 5 |  | 92 |
| 15 |  | 5 |  | 88 |
| 16 |  | 4 |  | 94 |
| 17 |  | 6 |  | 90 |
| 18 |  | 8 |  | 91 |
| 19 |  | 8 |  | 86 |
| 20 | PhCH(OH)Pr | 24 | No reaction | – |
| 21 | $Me_2CHOH$ | 24 | No reaction | – |

Table 1 *(Continued)*

| Entry | Substrate | Time(h) | Product | Yield (%) |
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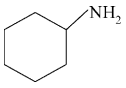
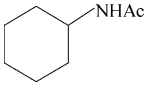
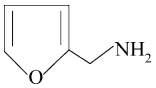
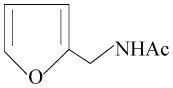
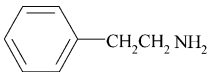
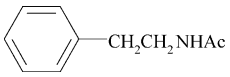
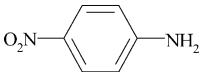
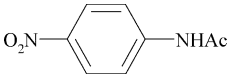
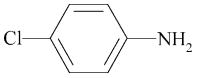
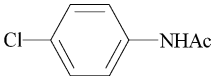
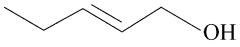
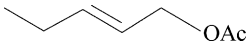
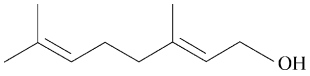
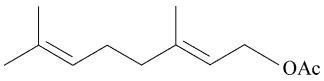
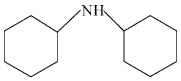
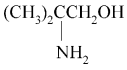
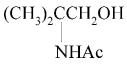
| 22 |  | 1 |  | 94 |
| 23 |  | 1 |  | 95 |
| 24 |  | 1 |  | 95 |
| 25 |  | 1 |  | 96 |
| 26 |  | 1 |  | 96 |
| 27 | $Me_3COH$ | 14 | $Me_2C{=}CH_2$ | 69 |
| 28 |  | 6 |  | 95 |
| 29 |  | 6 |  | 93 |
| 30 |  | 24 | No reaction | – |
| 31 | $HOCH_2CH_2NH_2$ | 16 | $HOCH_2CH_2NHAc$ | 85 |
| 32 |  | 16 |  | 80 |

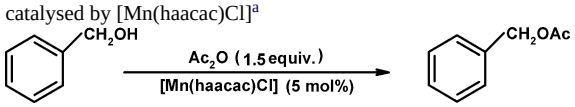
Isolated yields, all products gave satisfactory $^1$H NMR, IR and MS data.

$NO_2$, and $OCH_3$ (entries 4, 6, 25) also surveyed under the present reaction conditions.

Like primary alcohols (entries 1–12), primary amines (entries 22–26) were also acylated rapidly by this procedure. However, secondary amines did not undergo any change (entry 30). It is interesting note, in a competitive acylation reaction with an equimolar mixture of benzyl alcohol and benzyl amine by this procedure, the amine is acylated selectively while the alcohol is almost unaffected (acylation of OH group is less than 12% by $^1$H NMR). Thus, acylation of amino alcohols produced the corresponding acetamides only (entries 31, 32); the hydroxy moiety remained untouched. This selective acylation of a primary $NH_2$ over a primary OH by this process is one of considerable synthetic importance.

The effect of solvents on the reaction under the influence of 5 mol% of [Mn(haacac)Cl] is shown in Table 2. Under these conditions, the solvent effect on the catalytic reaction might depend on the polarity and coordinating property of these solvents. The reaction in nitromethane proceeds faster than other organic solvents and it was much slower in dimethylformamide and acetonitrile.

Table 2
Effect of solvents on acylation of benzyl alcohol using acetic anhydride catalysed by [Mn(haacac)Cl][a]




| Entry | Solvent | t/min | Conversion[b] (%) |
|---|---|---|---|
| 1 | $CH_3CN$ | 720 | 44.5 |
| 2 | DMF | 700 | 28.2 |
| 3 | $CHCl_3$ | 360 | 91.5 |
| 4 | $CH_2Cl_2$ | 360 | 90.6 |
| 5 | $Et_2O$ | 400 | 72.4 |
| 6 | THF | 400 | 74.3 |
| 7 | $PhCH_3$ | 400 | 79.6 |
| 8 | $CH_3NO_2$ | 360 | 96.4 |

[a] A solution of benzyl alcohol (0.25 M) was used.
[b] The conversion was determined by GC analysis of the crude product.

## 4. Conclusion

In conclusion, we have shown that bis(2-hydroxyanil) acetylacetonatomanganese(III)chloride complex is an efficient catalyst for acylation reactions of alcohols, amines and phenols. The notable advantages of this procedure are: (a) operational simplicity; (b) excellent selectivity for primary OH over secondary OH groups, and for $NH_2$ groups over NH and primary OH; (c) general applicability and (d) good yields.

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