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Mn(III) salen complex: an efficient reusable acylation catalyst☆

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Abstract

Acylation of alcohols in an efficient manner using [*N*,*N*′-ethylene bis(salicylideneaminato)] manganese(III) chloride [Mn(III) salen complex **1**] with anhydrides/acetic acid under novel heterogeneous media is reported for the first time.

Keywords: Acylation; Mn(III) salen complex; Heterogeneous catalysis; Alcohols

1. Introduction

Organic esters represent an important family of intermediates widely employed in the organic synthesis of fine chemicals, drugs, plasticizers, perfumes, food preservatives, cosmetics, pharmaceuticals, solvents and chiral auxillaries. Acylation of alcohols using acid anhydrides or acyl chlorides in the presence of stoichiometric amounts of amine bases such as tertiaryamines 4-(dimethylamino)pyridine [1], or 4-pyrrolidinopyridine [2] are well established procedures in the past. Some other procedures have also been developed wherein Lewis acid catalysts such as $TaCl_5$ [3], $CoCl_2$ [4], $Sc(OTf)_3$ [5–8], TMSOTf [9], Bu_3P [10,11] are involved in combination with Ac_2O. All these acid catalysts/reagents are incompatible to the substrates having double and triple bonds. Nevertheless, there is still a great demand for acid catalysts to generate esters under mild conditions. Some of these Lewis acid catalysts have also been used for chiral induction in presence of chiral ligands for non-enzymatic kinetic resolution of secondary alcohols [12–14].

The latest procedures reported the use of $Cu(OTf)_2$ [15] and $In(OTf)_3$ [16] as catalysts in esterification of alchols using acetic anhydride as acylating agent. These metal triflates are expensive, difficult to recover and reuse in the process. Moreover, employing acetic anhydride as acylating agent achieves less than 50% atom economy in the consumption of acetic anhydride by utilizing only the acyl group. These disadvantages have negative impact on the environment. Recent development of solid acids in the form of modified clays, montmorillonite K10, KSF [17,18] and metal exchanged montmorillonite [19] has positive impact in addressing the above problems.

The well known Kochi's Mn(III) salen catalyst **1** (Fig. 1) modified later by Jacobson and Katsuki whose preparation and handle are relatively easy, however, has not been utilized for the organic transformations other than oxidations [20–23]. In our earlier communications we have shown the Mn(III) salen complex **1** as efficient catalysts for Knoevenegel [24] and

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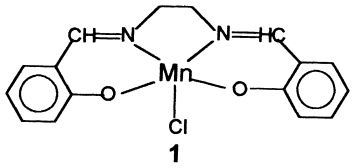

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Fig. 1. [*N*,*N*′-ethylene bis(salicylideneaminato)] manganese(III) chloride.

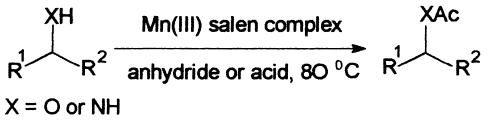
transesterification [25] reactions under reused conditions. During course of working on this catalyst **1** for various other organic transformations, we discovered Mn(III) salen complex **1** as an efficient and reusable catalyst for acylation of alcohols, phenols and amines. Herein we report acylation of phenols, amines and alcohols comprising primary, secondary, tertiary, benzylic and allylic in excellent yields using acetic acid or acetic anhydride as acylating agent catalysed by Mn(III) salen complex **1** for the first time (Scheme 1). The essential advantage of this reaction is recovery of the complex from the reaction medium by simple filtration, when reaction is conducted in a toluene solvent that renders the complex in suspended form.

2. Experimental section

2.1. Preparation of the catalyst

2.1.1. [N,N^1-ethylene bis(salicylideneaminato)] manganese(III) chloride (Mn(III) salen complex **1***)*

[*N*,*N*^{1}-ethylene bis(salicylideneaminato)] manganese(III) chloride was prepared by following Jacobsen's procedure [21]. The Mn(III) salen complex **1** was prepared from 6.127 g (25 mmol) of $Mn(OAc)_2{\cdot}4H_2O$ was added to 2.68 g (10 mmol) of salen ligand dissolved in ethanol (50 ml) and refluxed under air for 3 h at 80°C. 1.27 g (30 mmol) of LiCl was added to the above mixture, refluxed for a further period of 2 h and cooled in ice. The brown Mn salen complex **1** was filtered, washed with ethanol, ice-cold water and dried under vacuum for 6 h. Chemical analysis for $C_{16}H_{14}N_2O_2MnCl$: calcd Mn, 15.40; C, 53.9; H, 3.9; N, 7.8; Cl, 9.9; found Mn, 15.24; C, 51.8; H, 3.6; N, 7.2; Cl, 9.86. The complex was analyzed by UV and IR spectrometry and spectrum is similar to that of Kochi's [Mn(III) salen]$^+PF_6^-$ complex [20].



Scheme 1. Acylation of alcohols catalysed by Mn(III) salen complex.

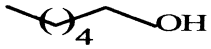
2.2. A typical experimental procedure for acylation reaction

Mn(III) salen complex **1** (25 mg, 0.07 mmol) was suspended in dry toluene (10 ml) followed by the addition of a mixture of benzyl alcohol (1 mmol, 0.108 g), acetic anhydride (1.5 mmol, 0.153 g) and heated to 80°C in two-necked round bottomed flask. The reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was filtered, washed with toluene, dried under vacuum and reused for next cycle. The filtrate was concentrated and purified by column chromatography (hexane/ethylacetate, 95/5, v/v) to afford the acetoxy methylbenzene (Table 2, entry 5a) as a colorless liquid, yield: 0.139 g (93%). ^{1}H NMR (200 MHz, Gemini Varian, using TMS as internal standard in $CDCl_3$) δ 2.08 (s, 3H), 5.09 (s, 2H), 7.30–7.35 (s, 5H); IR (neat, recorded on a Nicolet DX-5 spectrometer) cm^{-1}: 3050, 2960, 1740, 1458, 1220, 1010; MS [EI, 70 eV, scanned on VG 70–70H (micro mass)] *M*/*Z*: 150 [M^+ peak] (30), 108(100), 91(56), 43(48).

3. Results and discussion

Treatment of primary alcohol with 1.5 equivalents of acetic anhydride in presence of 5 mol% catalyst **1** in toluene at 80°C provided the corresponding acetate in qualitative yield (91–96%) (Table 2, entry 1a, 2, 3a, 4, 5a, 6). On the other hand, the reaction conducted at room temperature gave lower yields, i.e. 1-hexanol gave only 61% yield. Similarly treatment of secondary alcohols like menthol, cyclohexanol, 3-β-cholesterol and steroidal alcohol like anderosterone under similar conditions offered excellent yields (Table 3, entry 1a, 2a, 7, 8). It was noticed that phenol and 1-phenylethanol (Table 2, entry 11, Table 3, entry 6) require 3 equivalents of Ac_2O as to complete the reaction. Further tertiary alcohols are also cleanly,

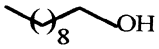
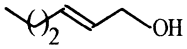
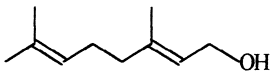
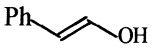
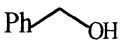
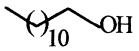
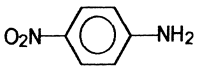
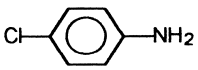
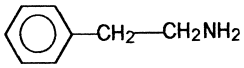
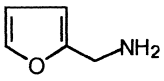
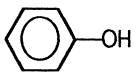
Table 1
Acylation of 1-hexanol using various anhydrides catalysed by Mn(III) salen complex **1**[a]

Entry	Substrate	Anhydride (equiv)	Time (h)	Yield (%)
1		Ac_2O(1.5)	1	91
2		Ac_2O(1.5)	6	61[b]
3		AcOH	8	94
4		$(EtCO)_2O$(1.5)	7	93
5		$(PrCO)_2O$(1.5)	9	96
6		$(BuCO)_2O$(1.5)	9	93
7		$(PhCO)_2O$(1.5)	10	95

[a] Isolated yields, all products gave satisfactory ^{1}H NMR, IR and MS data.
[b] Reaction conducted at room temperature.

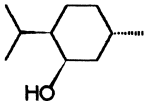
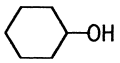
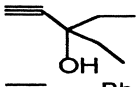
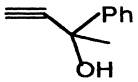
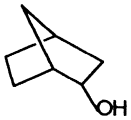
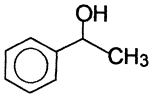
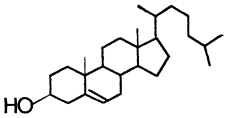
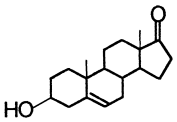
efficiently and rapidly converted into esters using catalyst **1** and Ac_2O (3 equiv) in toluene at 80°C. The treatment of 3-ethyl-1-pentyl-3-ol gave corresponding acetate 90%, whereas 2-phenyl-3-butyn-2-ol gave 75% yield (Table 3, entry 3, 4). It is significant to notice that tertiary alcohols are acylated to corresponding acetates selectively without any elimination product, while the acid sensitive substrates such as allylic and acetylenic alcohols undergo acylation without migration of double or triple bond, respectively (Table 2, entry 2, 3, 4; Table 3, entry 3, 4). Aromatic and aliphatic amines were also successfully acylated using Ac_2O (1.5 equiv) (Table 2, entry 7, 8, 9, 10). Finally, the acylation of 1-hexanol with higher acid anhydrides was also examined. Thus, 1-hexanol was

Table 2
Acylation of alcohols and amines using acetic acid or acetic anhydride catalysed by Mn(III) salen complex **1**

Entry	Substrate	Anhydride/acid	Time (h)	Yield (%)[a]
1a		Ac_2O(1.5)	6	94
1b		AcOH	12	87
2		Ac_2O(1.5)	6	96
3a		Ac_2O(1.5)	8	96
3b		AcOH	12	57
4		Ac_2O(1.5)	4	93
5a		Ac_2O(1.5)	6	93
5b		AcOH	12	92
6		Ac_2O(1.5)	5	96
7		Ac_2O(1.5)	1.5	93
8		Ac_2O(1.5)	1.0	97
9		Ac_2O(1.5)	0.5	96
10		Ac_2O(1.5)	0.5	93
11		Ac_2O(3.0)	4	92

[a] Isolated yields, all products gave satisfactory ^{1}H NMR, IR and MS data.

Table 3
Acylation of secondary and tertiary alcohols using acetic acid or acetic anhydride catalysed by Mn(III) salen complex **1**

Entry	Substrate	Anhydride/ acid	Time (h)	Yield (%)[a]
1a		Ac_2O(1.5)	4	96
1b		AcOH	12	93
2a		Ac_2O(1.5)	6	93
2b		AcOH	12	90
3		Ac_2O(3.0)	6	75
4		Ac_2O(3.0)	6	90
5		Ac_2O(1.5)	4	94
6		Ac_2O(3.0)	6	95
7		Ac_2O(1.5)	6	93
8		Ac_2O(1.5)	6	92

[a] Isolated yields, all products gave satisfactory ^{1}H NMR, IR and MS data.

reacted with propionic, buteric, valeric and benzoic anhydrides to the corresponding esters, respectively (Table 1, entry 4, 5, 6, 7) in excellent yields. In addition, chiral alcohols can also be acetylated easily in high yields with complete retention of optical activity (Table 2, entry 1a).

The above reaction when carried out using acetic acid as acylation agent afforded good yields albeit in longer time. The conversions are quite impressive for primary and secondary alcohols (Table 1, entry 3; Table 2, entry 1b, 5b; Table 3, entry 1b, 2b). Slightly low conversions were observed for allylic alcohols (Table 2, entry 3b) even at longer reaction time (12 h).

4. Conclusion

In conclusion, we have shown that Mn(III) salen complex **1** is an efficient and versatile catalyst for acylation reactions of alcohols, amines and phenol. The advantage of this method is that even hindered substrates can be acylated in high yield under mild conditions. The use of acetic acid rather than acetic anhydride is both economically and environmentally advantageous. Furthermore, the catalyst is readily recyclable via a simple filtration method. The resolution of racemic secondary alcohols with Jacobsen catalyst (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclo-hexane diamino-manganese(III) chloride, is under progress in our laboratory.

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