



Manganese(III) acetate as catalyst for the direct acetylation of alcohols with acetic acid

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Abstract

Manganese(III) acetate was found to catalyse the direct acetylation of primary, secondary and tertiary alcohols in presence of glacial acetic acid.

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1. Introduction

Esterification of carboxylic acids or acylation of alcohols are one of the fundamental processes in organic synthesis [1,2]. Direct acylation of alcohols or esterification of acids are usually carried out either in the presence of mineral acids or sulphonic acid. Esterifications with simple alcohols conveniently run by using large excess of alcohol as the solvent. The sulphuric acid catalyst is a strong dehydrating agent that helps to remove water as one of the side product.

This reaction is usually cannot be applied to the synthesis of esters from phenols and tertiary alcohols. The use of strong mineral acids leads to highly acidic waste streams posing an environmental problem for industrial processes.

In order to overcome this problem, acylation of alcohol is performed with activated acid anhydrides or acid chlorides [3]. Though the reaction works well, they are expensive when compared to those of carboxylic acids. Recently, Choudary et al. [4] have reported use of vanadyl (IV) acetate, a powerful Lewis acid, as a catalyst for the acetylation of primary, secondary and tertiary alcohols and steroidal alcohols in the presence of acetic anhydride in quantitative yields.

Lee and Park [5] have reported metallic Lewis acids catalysed acetylation of alcohols with acetic anhydride and acetic acid in ionic liquids. Barrett and Braddock [6] used scandium (III) or lanthanide (III) triflates as a catalyst for the acetylation of alcohols in the presence of acetic acid. Most of these methods suffer from inherent disadvantages such as high cost of the catalyst, elimination by-products in tertiary alcohols and tedious working up procedures, etc.

Mn(III) acetate have found increasing use as a mild and selective reagent in organic synthesis, being used as an oxidising agent in synthesising different class of compounds [7–10]. For instance, Mn(III) acetate is extensively used for oxidising olefins to γ -lactones. During the process of this reaction the allylic acetate is formed as a minor product [9].

2. Results and discussion

In the course of our studies on the application of Mn(III) acetate reagent in the organic synthesis we found that this reagent actively catalyses acetylation of alcohols. Herein we report the direct acylation of primary, secondary and tertiary alcohols using catalytic amount of Mn(III) acetate dihydrate. The use of acetic acid rather than acetic anhydride or acetyl chloride is economically and environmentally advantageous. Furthermore this catalyst is commercially available or can be prepared in laboratory [7] and can be stored for an extended period of time [9].

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Table 1

The representative alcohol used for the acetylation in presence of catalytic amount of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ $\xrightarrow[\text{CH}_3\text{COOH, Reflux}]{\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}}$ R-OAc

S. no.	Alcohol (R-OH)	Product (R-OAc)	Yield (%)
1			99
2			99
3			99
4			99
5			99
6			99
7			99
8			99
9			99

The experimental procedure for these acetylations is very simple and does not require any inert atmosphere. In a typical experiment a catalytic amount of Mn(III) acetate dihydrate was added to a stirred solution of alcohol with acetic acid. Acetylation occurs with quantitatively within 2 h at reflux temperature. Even the tertiary alcohol like *t*-butanol can be acetylated with the same rate/ease as other primary alcohols. In the control experiments with no Mn(III) acetate dihydrate only small amount of the alcohols were converted to their acetates in the same reaction time. Table 1 (entries 1–9) shows representative alcohols used for the reaction.

All the isolated products were characterised by spectral studies (viz. IR, ^1H NMR) the spectra were comparable with those of standard esters.

3. Experimental section

3.1. General remarks

All reactions were carried out in oven dried glassware. IR spectra were recorded using Biorad FT-IR spectrometer, ^1H NMR spectra were recorded in CDCl_3 using a 60 MHz FT-NMR spectrometer. All other chemicals were purchased from commercial suppliers and were used as received.

3.2. General procedure for the preparation of esters

In a typical experiment a catalytic amount of Mn(III) acetate dihydrate (0.04 mmol) was added to a stirred solution of alcohol (10 mmol) in acetic acid (10 ml). Acetylation occurs quantitatively within 2 h at reflux temperature. Isolation of the acetylated product includes cooling of the reaction mixture to room temperature, extraction with diethyl ether, washing the diethyl ether to neutral, drying over anhydrous sodium sulphate and finally removing diethyl ether under reduced pressure. The products were characterised by IR and ^1H NMR.

4. Conclusion

In conclusion we have demonstrated the use of Mn(III) acetate dihydrate as a catalyst in acetylation of alcohols including primary, secondary and tertiary alcohols.

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