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Rapid and efficient acetylation of alcohols and phenols with acetic anhydride catalyzed by electron-deficient tin(IV) porphyrin

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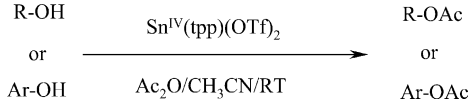
Abstract

Rapid and efficient esterification of alcohols and phenols with acetic anhydride was achieved in the presence of tin(IV) tetraphenylporphyrinato trifluoromethanesulfonate, $Sn^{IV}(tpp)(OTf)_2$, as a catalyst. The remarkably high catalytic activity of $Sn^{IV}(tpp)(OTf)_2$ can be used to assist the acetylation of not only primary alcohols but also sterically-hindered secondary and tertiary alcohols with acetic anhydride. This catalyst can also catalyze the acetylation of phenols with acetic anhydride.

1. Introduction

Developing efficient and mild methods for the protection of hydroxyl group of alcohols and phenols is of great importance in synthetic organic chemistry. One of the most common methods for the protection of these compounds is the formation of acetyl derivatives [1]. The protection of such functional groups is often necessary during the course of various transformations in a synthetic sequence, especially in the construction of polyfunctional molecules such as nucleosides, carbohydrates, steroids and natural products. A number of procedures are available for the preparation of acetyl derivatives, including homogeneous and heterogeneous reagents such as 4-(dimethylamino)pyridine and 4-pyrolidinopyridine [2], *N*,*N*,*N*′,*N*′-tetramethylethylenediamine [3], tributylphosphine [4], iodine [5], *p*-toluenesulfonic acid [6], alumina [7], zinc chloride [8], cobalt chloride [9], montmorillonite K-10 and KSF [10], zeolite HSZ-360 [11], zirconium sulfophenyl phosphonate [12], scandium trifluoromethanesulfonate [$Sc(OTf)_3$] [13], $TaCl_5$ [14], trimethylsilyl trifluoromethanesulfonate (TMSOTf) [15], copper trifluoromethansulfonate [$Cu(OTf)_2$] [16], indium trifluoromethanesulfonate [$In(OTf)_3$] [17], magnesium bromide [18], bismuth(III) salts [19], ferric perchlorate adsorbed on silica-gel [20] and tin(IV) tetraphenylporphyrin perchlorate [21]. However, some of the reported methods for the acetylation of alcohols suffer from one or more of the following disadvantages such as high temperature and drastic reaction conditions, formation of undesirable or toxic byproducts, expensive reagents, hygroscopicity and thermal instability of the reagents, long reaction times, low yields of the desire products and bulk requirements of solid bed. Therefore, introduction of new methods and catalysts for the preparation of esters is still in demand.

The successful use of metalloporphyrins as mild Lewis acid catalysts [21,22] prompted us to explore the potential of these complexes for catalysts for the conversion of alcohols and phenols to their corresponding esters. Here, we wish to report a simple, rapid and efficient method for the acetylation of alcohols and phenols with acetic anhydride catalyzed by tin(IV) tetraphenylporphyrinato trifluoromethanesulfonate, $Sn^{IV}(tpp)(OTf)_2$, at room temperature (Scheme 1).



Scheme 1.

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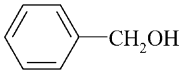
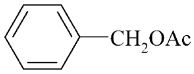
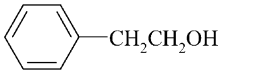
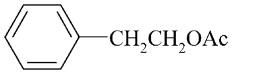
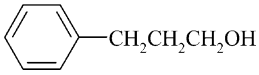
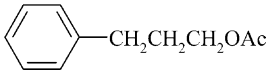
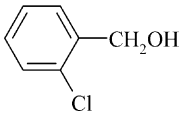
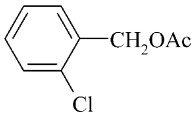
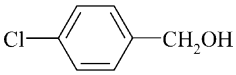
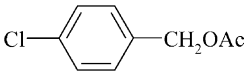
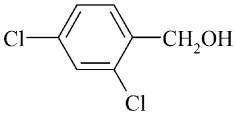
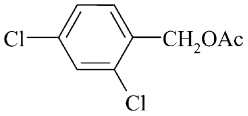
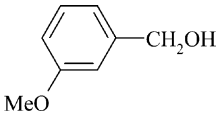
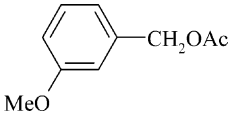
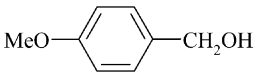
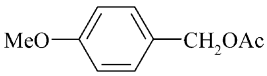
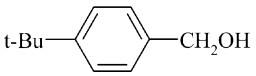
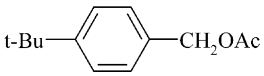
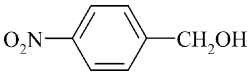
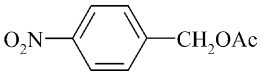
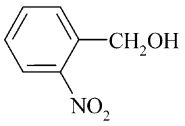
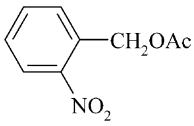
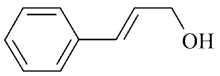
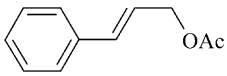
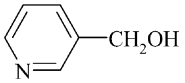
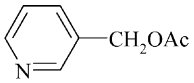
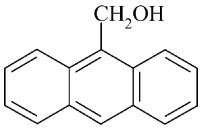
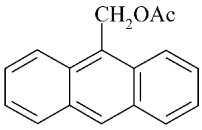
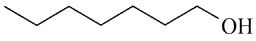
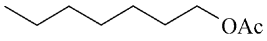
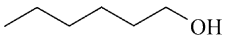
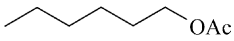
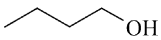
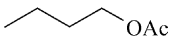
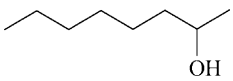
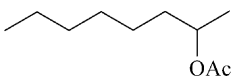
Table 1
Acetylation of alcohols with Ac_2O catalyzed by $Sn^{IV}(tpp)(OTf)_2$ at room temperature

Entry	Substrate	Product	Time (min)	Yield (%)[a]
1			1	95
2			1	94
3			1	95
4			1	93
5			1	92
6			1	93
7			1	95
8			1	92
9			1	90
10			1	89
11			1	92
13			1	91
14			1	90
15			5	95
16			1	88
17			1	89
18			1	87
19			1	90

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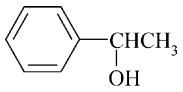
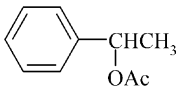
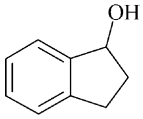
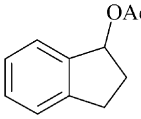
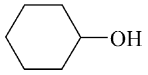
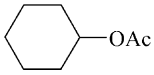
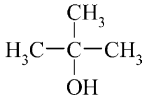
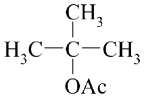
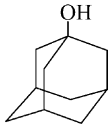
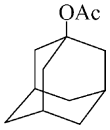
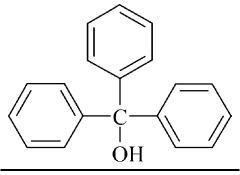
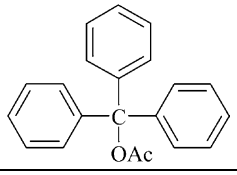
20			1	93
21			1	90
22			1	90
23			1	88
24			1	90
25			15	95

[a] Isolated yields.

Table 2
Acetylation of phenols with Ac_2O catalyzed by $Sn^{IV}(tpp)(OTf)_2$ at room temperature

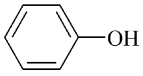
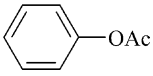
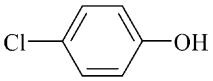
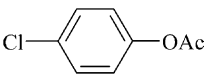
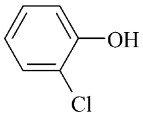
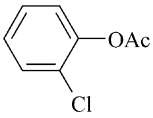
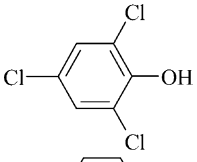
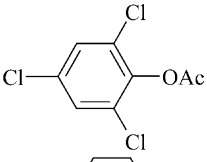
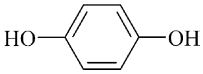
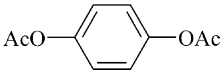
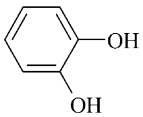
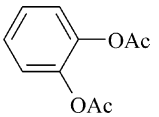
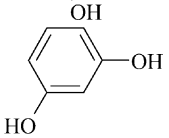
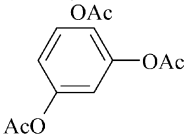
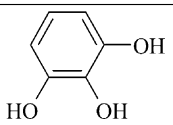
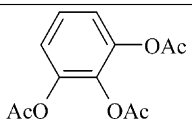
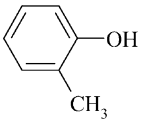
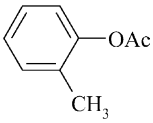
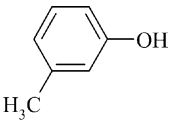
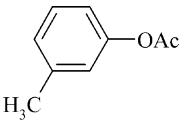
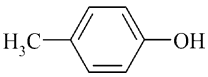
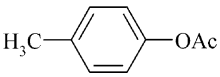
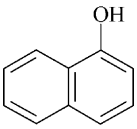
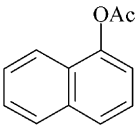
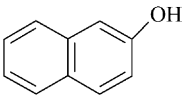
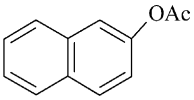
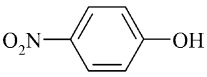
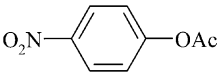
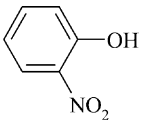
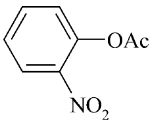
Entry	Substrate	Product	Time (min)	Yield (%)[a]
1			1	94
2			1	92
3			1	91
4			1	93
5			1	94
6			1	90
7			1	91

Table 2 (*Continued*)

Entry	Substrate	Product	Time (min)	Yield (%)[a]
8			1	93
9			1	90
10			1	93
11			1	91
12			1	95
13			1	93
14			1	91
15			15	85

[a] Isolated yields.

Table 3
Competitive acetylation of alcohols, acetals and silyl ethers catalysed by $Sn^{IV}(tpp)(OTf)_2$

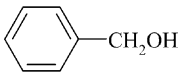
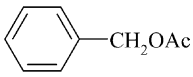
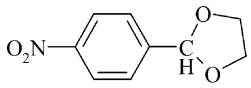
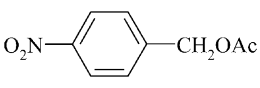
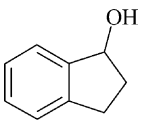
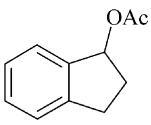
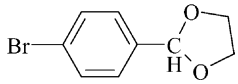
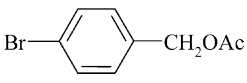
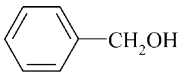
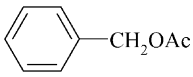
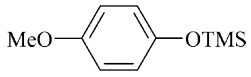
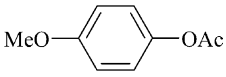
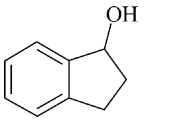
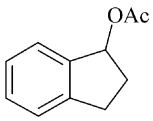
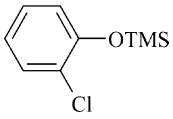
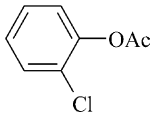
Run	Substrate	Product	Time (min)	Yield (%)[a]
1			1	99
			1	0
2			1	99
			1	0
3			1	99
			1	0

Table 3 (*Continued*)

Run	Substrate	Product	Time (min)	Yield (%)[a]
4			1	99
			1	0

[a] GC yields.

2. Results and discussions

2.1. Acetylation of alcohols with acetic anhydride catalyzed by $Sn^{IV}(tpp)(OTf)_2$

Initially, benzyl alcohol (1 mmol) was chosen as a model substrate for the acylation reaction. The reaction of this alcohol with acetic anhydride (2 equivalent) in acetonitrile (2 mL) in the presence of 0.01 molar equivalent of $Sn^{IV}(tpp)(OTf)_2$ at room temperature was completed in 1 min and the corresponding acetate was obtained in 99% yield. In the absence of $Sn^{IV}(tpp)(CF_3SO_3)_2$, the reaction was much less efficient.

As shown in Table 1, a series of primary alcohols (including aliphatic and aromatic alcohols) and secondary alcohols were acetylated with acetic anhydride in the presence of 0.01 molar equivalent of $Sn^{IV}(tpp)(CF_3SO_3)_2$ at room temperature in 99% yields. Tertiary alcohols (such as 1-adamantanol, *t*-butanol, and triphenylmethanol) were also acetylated in high yields, without the formation of dehydration products (entries 23–25).

2.2. Acetylation of phenols with acetic anhydride catalyzed by $Sn^{IV}(tpp)(OTf)_2$

We extended the scope of this transformation by performing the reaction of phenols with acetic anhydride (2 equivalent for each hydroxyl group) in acetonitrile (2 mL). At room temperature and in the presence of 0.01 molar equivalent of the catalyst, phenols were converted to their corresponding acetates in excellent yields (Table 2). The acetylation of polyhydroxy phenols was also investigated and the corresponding polyacetates were obtained in 99% yields (Table 2, entries 5–8).

In comparison with the data reported with $Sn^{IV}(tpp)(ClO_4)_2$ catalyst [21], these results clearly indicate that $Sn^{IV}(tpp)(CF_3SO_3)_2$ is a more powerful catalyst for the acetylation of alcohols and phenols.

In order to check the selectivity of the described method, we have also investigated the competitive acetylation of alcohols with acetals and silyl ethers. The results showed that alcohols were acetylated selectively in the presence of acetals and silyl ethers (Table 3). This may be considered as a useful practical achievement in esterification reactions.

3. Conclusion

Although metalloporphyrins are widely used as redox catalysts, there have been few studies on their catalytic activity as Lewis acids. In this report, we have demonstrated that the tin(IV) tetraphenylporphyrinato trifluoromethanesulfonate, $Sn^{IV}(tpp)(OTf)_2$, which is a stable Sn(IV) compound, can be considered as a mild Lewis acid for efficient and catalytic acetylation of alcohols and phenols. The advantage of this system is that even hindered substrates can be acetylated with acetic anhydride in high yields at room temperature. In addition, low reaction times, non-toxicity, ease of preparation of the catalyst make this method a useful addition to the methodologies.

4. Experimental

Chemicals were purchased from Fluka and Merck chemical companies. ^1H NMR spectra was recorded in $CHCl_3$ solvent on a Bruker AM 80 MHz spectrometer using TMS as an internal standard. Infrared spectra were run on a Philips PU9716 or Shimadzu IR-435 spectrophotometer. All analyses were performed on a Shimadzu GC-16A instrument with a flame ionization detector using silicon DC-200 or Carbowax 20-M columns. Tetraphenylporphyrin was prepared and metallated according to the literature [23,24].

4.1. Preparation of tin(IV) tetraphenyporphyrinato trifluoromethanesulfonate, $Sn^{IV}(tpp)(OTf)_2$

To a solution of $Sn(tpp)Cl_2$ (1.03 g, 1 mmol) in 100 mL of THF, at 55 °C, $AgCF_3SO_3$ (0.54 g, 2 mmol) was added. The solution was stirred at 55 °C for 30 min. The AgCl precipitate was filtered through a 0.45 μM filter. The resulting solution was evaporated moderately. $Sn^{IV}(tpp)(OTf)_2$ was then extracted with CH_2Cl_2. The $Sn^{IV}(tpp)(OTf)_2$ crystals was obtained by evaporation of solvent at room temperature.

4.2. General procedure for acetylation reactions

In a round-bottom flask (25 mL) equipped with a magnetic stirrer, a solution of alcohol or phenol (1 mmol) in Ac_2O (2 equivalent for each OH group of alcohol or phenol) and CH_3CN (2 mL) was prepared. $Sn^{IV}(tpp)(OTf)_2$ (0.010 g, 0.01 mmol) was added to this solution and the reaction mixture was stirred at room temperature. The reaction was monitored by GLC. After completion of the reaction, the mixture was directly passed through a short column of silica-gel (hexane:ethyl acetate = 1:1) 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.

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