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Electron-deficient [Ti^{IV}(salophen)(OTf)$_2$]: A new and highly efficient catalyst for the acetylation of alcohols and phenols with acetic anhydride

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ABSTRACT

In the present work, a highly efficient method for acetylation of alcohols and phenols with acetic anhydride catalyzed by high-valent [Ti^{IV}(salophen)(OTf)$_2$] is reported. Under these conditions, primary, secondary and tertiary alcohols as well as phenols were acetylated with short reaction times and high yields. The catalyst was reused several times without loss of its catalytic activity.

1. Introduction

Schiff base complexes of Mn, Fe, Ru, Cr, Co and V have found many applications in organic chemistry [1]. These compounds have been used as catalysts in the oxidation of alkenes, alkanes, sulfides, amines and alcohols. Titanium Schiff bases have been used as catalysts for the polymerization of ethylene and propene [2], regio- and stereoselective epoxidation of allylic alcohols [3], asymmetric ring-opening of epoxides by dithiophosphorus acid [4], enantioselective catalytic ring-opening of epoxides with carboxylic acids [5], efficient kinetic resolution of terminal epoxides by means of catalytic hydrolysis [6], enantioselective trimethylsilylcyanation of aldehyde [7,8], oxidation of sulfides to sulfoxides with hydrogen peroxide [9], enantioselective ring-opening of *meso*-epoxides with ArSH [10], asymmetric alkynylation of aldehydes [11] and enantioselective Pinacol coupling of aryl aldehydes [12].

The protection of hydroxyl groups is often necessary during the course of various transformations in a synthetic sequence, especially in the synthesis of fine chemicals and natural products. Several methods, such as acetylation, tetrahydropyranylation, methoxymethylation and trimethylacetylation, have been reported for the protection of hydroxyl groups [13,14]. A variety of procedures using homogeneous or heterogeneous catalysts such as iodine [15], *p*-toluenesulfonic acid [16], alumina [17], zinc chloride [18], cobalt chloride [19], montmorillonit K-10 and KSF [20], zeolite HSZ-360 [21], zirconium sulfophenyl phosphonate [22], Sc(OTf)$_3$ [23], TaCl$_5$ [24], TMSOTf [25], Cu(OTf)$_2$ [26], In(OTf)$_3$ [27], magnesium bromide [28], bismuth(III) salts [29], ferric perchlorate adsorbed on silica-gel [30], RuCl$_3$ [31], InCl$_3$ [32], Ce(OTf)$_3$ [33], Mg(ClO$_4$)$_2$ [34], ZrCl$_4$ [35], Cp$_2$ZrCl$_2$ [36], ZrOCl$_2$·8H$_2$O [37], Al(OTf)$_3$ [38], NaHSO$_4$·SiO$_2$ [39], La(NO$_3$)$_3$·6H$_2$O [40], NbCl$_5$ [41], Gd(OTf)$_3$ [42], Alumina supported MoO$_3$ [43] cerium polyoxometallate [44], Zn(ClO$_4$)$_2$·6H$_2$O [45], Mg(NTf$_2$)$_2$ [46], Cu(BF$_4$)$_2$ [47], BiO(ClO$_4$)$_2$ [48], HClO$_4$–SiO$_2$ [49], HBF$_4$–SiO$_2$ [50], ZrO(OTf)$_2$ [51], Cp$_2$Ti(OSO$_2$C$_8$F$_{17}$)$_2$ [52], Cp$_2$Zr(OSO$_2$C$_8$F$_{17}$)$_2$ [53] and electron-deficient tin (IV) porphyrins [54–56] and have been routinely reported for the acetylation of alcohols and phenols with Ac$_2$O. Although these procedures provide an improvement, many of these catalysts or activators need long reaction times, drastic reaction conditions or tedious workups, and the catalysts are moisture sensitive or expensive. Hence new procedures to circumvent these problems are still in demand.

Electron-deficient complexes of Fe, Cr and Sn have been used as mild Lewis acids in organic transformations [54–70]. In this paper we report a rapid and highly efficient method for the acetylation of alcohols and phenols with acetic anhydride catalyzed by high-valent titanium(IV) salophen trifluoromethanesulfonate, [Ti^{IV}(salophen)(OTf)$_2$], at room temperature (Scheme 1).

2. Experimental

Chemicals were purchased from Merck or Fluka chemical companies. FT-IR spectra were obtained with potassium bromide pel-

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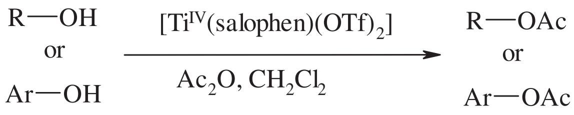


Scheme 1. Acetylation of alcohols and phenols with Ac_2O catalyzed by [Ti^{IV}(salophen)(OTf)$_2$].

lets in the range 400–4000 cm^{-1} with a Nicolet Impact 400D spectrometer. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20M. In the GC experiments, *n*-decane was used as an internal standard. ^{1}H NMR spectra were recorded on a Bruker-Avance AQS 400 MHz spectrometer.

2.1. The preparation of the catalyst

2.1.1. Preparation of [Ti^{IV}(salophenCl$_2$]

In a typical procedure, a solution of $TiCl_4(THF)_2$ (669 mg, 2.0 mmol) in dry THF (10 mL) was added slowly to a solution of H$_2$Salophen (633 mg, 2.0 mmol) in THF (10 mL), resulting in a red-brown solution. The reaction mixture was stirred and refluxed at 70 °C for 1 h, then cooled to room temperature, and the solvent was evaporated. The solid was slurried with Et_2O (20 mL), filtered through a fine-fritted funnel, washed with additional Et_2O, and dried under vacuum at 80 °C for 2 h [71].

2.1.2. Preparation of [Ti^{IV}(salophen)(OTf)$_2$]

To a solution of [Ti^{IV}(salophen)Cl$_2$] (434 mg, 1 mmol) in CH_2Cl_2 (15 mL) was added an acetonitrile solution (15 mL) of AgOTf (513.9 mg, 2 mmol), producing a brown precipitate. The AgCl that formed was filtered off through a fine fritted funnel, and the filtrate was concentrated to dryness. The solid was extracted with CH_2Cl_2 and the resulting solid was isolated [71].

^{1}H NMR (400 MHz, CD_3OD) δ: 9.44 (s, 2H, H–C=N), 8.10 (dd, 2H, Ar, ^1J = 6.2, ^2J = 3.2 Hz), 7.95 (d, 2H, Ar, J = 7.6 Hz), 7.72 (m, 2H, Ar), 7.64 (dd, 2H, Ar, ^1J = 6.4, ^2J = 3.2 Hz), 7.18 (m, 2H, Ar), 6.96 (d, 2H, Ar, J = 8 Hz); ^{13}C NMR (CD_3OD) δ: 116.53, 117.24 (CH), 117.58 (O–C–C), 121.24 (CF_3), 123.62, 130.41, 136.37, 138.10 (CH), 141.46 (N–C), 160.56 (O–C), 161.64 (N=CH).

2.2. General procedure for the acetylation of alcohols and phenols with Ac_2O catalyzed by [Ti^{IV}(salophen)(OTf)$_2$]

To a solution of alcohol or phenol (1 mmol) and Ac_2O (3 mmol per OH group) in CH_2Cl_2 (1 mL) was added [Ti^{IV}(salophen)(OTf)$_2$] (2 mol%) and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by GC. After completion of the reaction, the solvent was evaporated, Et_2O (10 mL)

Table 1
Optimization of the catalyst amount in the acetylation of 4-chlorobenzyl alcohol with Ac_2O catalyzed by [Ti^{IV}(salophen)(OTf)$_2$] at room temperature.[a]

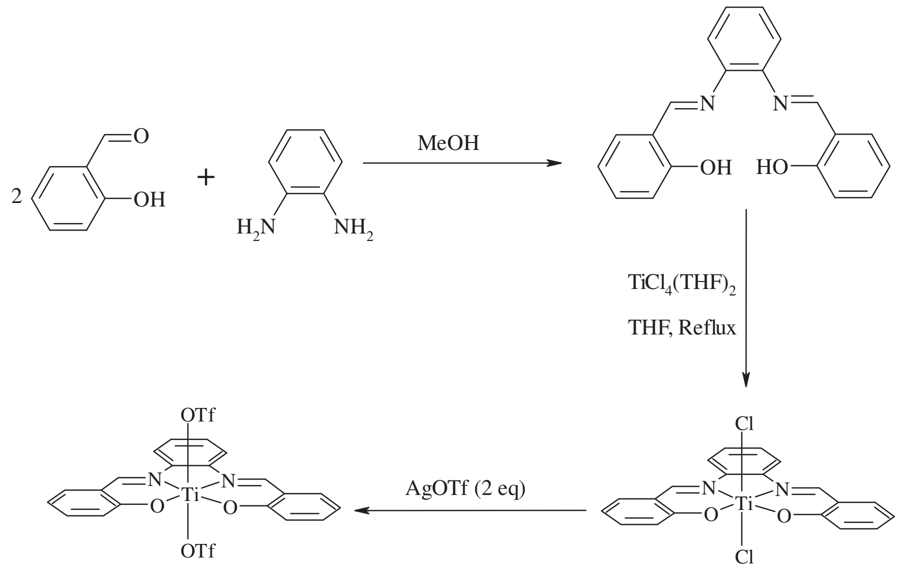
Entry	Catalyst amount (%mol)	Solvent	Time (min)	Yield (%)[b]
1	1	CH_3CN	8	56
2	2	CH_3CN	8	71
3	3	CH_3CN	8	95
4	1	CH_2Cl_2	1	77
5	2	CH_2Cl_2	1	100
6	3	CH_2Cl_2	1	100
7	2	*n*-Hexane	1	18
8	2	$CHCl_3$	1	25

[a] *Reaction conditions*: alcohol (1 mmol), acetic anhydride (3 mmol), solvent (1 ml).
[b] GC yield.

Table 2
Optimization of the Ac_2O amount in the acetylation of 4-chlorobenzyl alcohol.[a]

Entry	Time (min)	Ac_2O (mmol)	Yield (%)[b]
1	1	0.5	18
2	1	1.0	34
3	1	1.5	54
4	1	2.0	72
5	1	2.5	91
6	1	3.0	100

[a] *Reaction conditions*: alcohol (1 mmol), Ac_2O, catalyst (2 mol%), CH_2Cl_2 (1 mL).
[b] GC yield.



Scheme 2. The preparation route for the catalyst.