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Highly efficient and chemoselective trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS) catalyzed by reusable electron-deficient [Ti^{IV}(salophen)$(OTf)_2$]

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ABSTRACT

In the present work, highly efficient trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS) catalyzed by high-valent [Ti^{IV}(salophen)$(OTf)_2$] is reported. Under these conditions, primary, secondary and tertiary alcohols as well as phenols were silylated in short reaction times and high yields. It is noteworthy that this method can be used for chemoselective silylation of primary alcohols in the presence of secondary and tertiary alcohols and phenols. The catalyst was reused several times without loss of its catalytic activity.

1. Introduction

The protection of hydroxyl groups is an important reaction especially in the synthesis of fine chemicals and natural products. Several methods such as acetylation, tetrahydropyranylation, methoxymethylation and trimethylsilylation have been reported for protection of hydroxyl groups [1,2]. The common method for the silylation of hydroxy functional groups is the use of hexamethyldisilazane (HMDS). One disadvantage of HMDS is its poor silylating power in the absence of a suitable catalyst which needs forceful conditions and long reaction times in many cases [3]. To solve this problem, a variety of catalysts including $(CH_3)_3SiCl$ [4], $ZrCl_4$ [5], $ZnCl_2$ [6], K-10 montmorillonite [7], $LiClO_4$ [8], $H_3PW_{12}O_{40}$ [9], iodine [10], $InBr_3$ [11], zirconium sulfophenyl phosphonate [12], $CuSO_4{\cdot}5H_2O$ [13], sulfonic acid-functionalized nanoporous silica [14], $MgBr_2{\cdot}OEt_2$ [15], $LaCl_3$ [16], poly(*N*-bromobenzene-1,3-disulfonamide) and *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide [17], $Fe(TFA)_3$ [18], Fe_3O_4 [19], (n-Bu_4N)Br [20], trichloroisocyanuric acid (TCCA) [21], $HClO_4$–SiO_2 [22], Pd [23], $ZrO(OTf)_2$ [24], $LiClO_4$–SiO_2 [25], $PhMe_3N^+Br_3^-$ [26], poly(4-vinylpyridinium tribromide) [27], 1,3-dichloro-5,5-dimethylhydantoin (DCH) and/or trichloromelamine (TCM) [28] sulfamic acid [29] and H_5IO_6/KI [30] have been reported for trimethylsilylation of alcohols and phenols. Although these procedures provide an improvement, many of these catalysts or activators need long reaction times, drastic reaction conditions or tedious work up, or are moisture sensitive or expensive. Hence, introduction of new procedures to circumvent these problems is still in demand.

Schiff base complexes of Mn, Fe, Ru, Cr, Co and V have found many applications in organic chemistry [31]. These compounds have been used as catalyst in the oxidation of alkenes and alkanes, sulfides, amines and alcohols. Titanium Schiff bases have been used as catalyst for polymerization of ethylene and propene [32], regio- and stereoselective epoxidation of allylic alcohols [33], asymmetric ring-opening of epoxides by dithiophosphorus acid [34], enantioselective catalytic ring-opening of epoxides with carboxylic acids [35], efficient kinetic resolution of terminal epoxides by means of catalytic hydrolysis [36], enantioselective trimethylsilylcyanation of aldehydes [37,38], oxidation of sulfides to sulfoxides with hydrogen peroxide [39], enantioselective ring-opening of *meso*-epoxides with ArSH [40], asymmetric alkynylation of aldehydes [41] and enantioselective Pinacol coupling of aryl aldehydes [42].

Electron-deficient complexes of Fe, Cr, Sn and V have been used as mild Lewis acids in organic transformations [43–60]. In this paper, we report the use of high-valent titanium(IV)salophen trifluoromethanesulfonate, [Ti^{IV}(salophen)$(OTf)_2$], in the rapid and highly efficient silylation of alcohols and phenols with HMDS at room temperature (Scheme 1).

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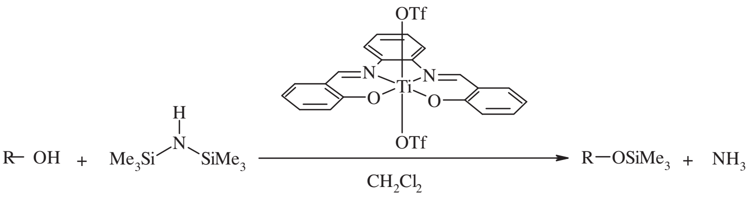


Scheme 1. Trimethylsilylation of alcohols and phenols with HMDS catalyzed by [Ti^{IV}(salophen)$(OTf)_2$].

Table 1
Optimization of catalyst amount in the silylation of benzyl alcohol with HMDS catalyzed by [Ti^{IV}(salophen)$(OTf)_2$] at room temperature.[a]

Entry	Catalyst amount (%mol)	Solvent	Time (min)	Yield (%)[b]
1	1	CH_3CN	1	44
2	2	CH_3CN	1	56
3	3	CH_3CN	1	79
4	0	CH_2Cl_2	1	16
5	0.1	CH_2Cl_2	1	33
6	0.1	CH_2Cl_2	10	47
7	0.5	CH_2Cl_2	1	42
8	1	CH_2Cl_2	1	75
9	2	CH_2Cl_2	1	100
10	3	CH_2Cl_2	1	100
11	2	EtOAc	1	37
12	2	*n*-Hexane	1	15
13	2	$CHCl_3$	1	30

[a] Reaction conditions: benzyl alcohol (1 mmol), HMDS (0.7 mmol), solvent (1 mL).

[b] GC yield.

2. Experimental

vAll chemicals were purchased from Merck or Fluka chemical companies. FT-IR spectra were obtained with potassium bromide pellets 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 20 m. In the GC experiments, *n*-decane was used as an internal standard. ^1H NMR spectra were recorded on a Bruker-Avance AQS 400 MHz spectrometer.

2.1. Preparation of [Ti^{IV}(salophen)Cl_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_2Salophen (633 mg, 2.0 mmol) in THF (10 mL), resulting in a red-brown solution. The reaction mixture was stirred under reflux at 70 °C for 1 h, and 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 [61].

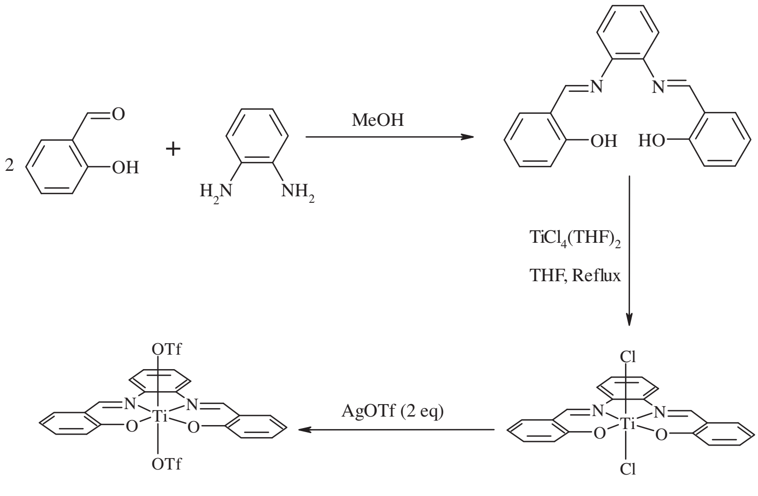
2.2. Preparation of [Ti^{IV}(salophen)$(OTf)_2$]

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 was filtered 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 [61].

^1H NMR (400 MHz, CD_3OD) $\delta = 9.44$ (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 (100 MHz, CD_3OD) $\delta = 116.53$, 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). IR (KBr): ν(CC=N) 1603, ν(SC=O) 1168 and ν(C–F) 1280.

2.3. General procedure for trimethylsilylation with HMDS catalyzed by [Ti^{IV}(salophen)$(OTf)_2$]

To a mixture of alcohol or phenol (1 mmol), HMDS (0.7 mmol per OH group) in CH_2Cl_2 (1 mL) was added [Ti^{IV}(Salophene)$(OTf)_2$] (0.01 mmol) and stirred at room temperature for appropriate time



Scheme 2. The preparation route for catalyst.