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$[Sn^{IV}(TPP)(BF_4)_2]$: An efficient and reusable catalyst for chemoselective trimethylsilylation of alcohols and phenols with hexamethyldisilazane

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ABSTRACT

Tin(IV)tetraphenylporphyrinato tetrafluoroborate, $[Sn^{IV}(TPP)(BF_4)_2]$, was used as an efficient catalyst for trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS). High-valent $[Sn^{IV}(TPP)(BF_4)_2]$ catalyzes trimethylsilylation of primary, secondary and tertiary alcohols as well as phenols, and the corresponding TMS-ethers were obtained in high yields and short reaction times at room temperature. While, under the same reaction conditions $[Sn^{IV}(TPP)Cl_2]$ is less efficient to catalyze these reactions. One important feature of this catalyst is its ability in the 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 functional groups is often necessary during the course of various transformations in a synthetic sequence, especially in the synthesis of fine chemicals and natural products [1–3]. Hydroxy functional group, which is a versatile functional group, can be protected by a wide variety of methods such as tetrahydropyranylation, acetylation, methoxymethylation and trimethylsilylation. Commonly, silyl ethers are prepared by treatment of hydroxyl compounds with silyl chlorides or silyl triflates in the presence of bases such as imidazole [4], 4-(*N*,*N*-dimethylamino)pyridine [5], *N*,*N*-diisopropylethylamine [6] and Li_2S [7]. However, some of these silylation methods suffer from disadvantages such as the lack of reactivity or the difficulty in removal of amine salts derived during the silylation reaction. To overcome these problem, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), which is a stable, commercially available and cheap reagent, is used for preparation of silyl ethers from hydroxyl compounds. This silylation method does not need special precautions and produces ammonia as by-product, but silylation in the absence of a suitable catalyst needs forceful conditions and long reaction times [8]. In order to increase the silylating power of HMDS, a variety of catalysts including trichloroisocyanuric acid (TCCA) [9], silica supported perchloric acid ($HClO_4$–SiO_2) [10], $ZrCl_4$ [11], K-10 montmorilonite [12], $LiClO_4$ [13], $H_3PW_{12}O_{40}$ [14], iodine [15], $InBr_3$ [16], zirconium sulfophenyl phosphonate [17], $CuSO_4 \cdot 5H_2O$ [18], sulfonic acid-functionalized nanoporous silica [19], $MgBr_2 \cdot OEt_2$ [20], $LaCl_3$ [21], poly(*N*-bromobenzene-1,3-disulfonamide) and *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonamide [22], $Fe(TFA)_3$ [23], Fe_3O_4 [24], $(n\text{-}Bu_4N)Br$ [25] and $ZrO(OTf)_2$ [26] have been reported. Although these procedures provide an improvement, but many of these catalysts need long reaction times, drastic reaction conditions or tedious workups, moisture sensitive or expensive of the catalyst. Hence, introduction of new procedures to circumvent these problems is still in demand.

Electron-deficient metalloporphyrins have been used as mild Lewis acids catalysts [27–32]. Recently, chromium and iron porphyrins have been used for organic transformations. Chromium(III) tetraphenylporphyrinato chloride, Cr(tpp)Cl, has been applied for regio-selective [3,3] rearrangement of aliphatic allyl vinyl ethers and for Claisen rearrangement of simple aliphatic allyl vinyl ethers. Iron(III)tetraphenylporphyrinato triflate, Fe(tpp)OTf, has been used for rearrangement of α,β-epoxy ketones into 1,2-diketones and chromium(III)tetraphenylporphyrinato triflates, Cr(tpp)OTf, has been reported for highly regio- and stereoselective rearrangement of epoxides to aldehydes [33–36].

Recently, we have reported the use of tin(IV)tetraphenylporphyrinato perchlorate [37,38], tin(IV)tetraphenylporphyrinato trifluoromethanesulfonate [39,40], and tin(IV)tetraphenylporphyrinato tetrafluoroborate [41,42] in organic synthesis.

In this paper, we wish to report a rapid and highly efficient method for trimethylsilylation of alcohols and phenols with hexamethyldisilazane catalyzed by high-valent $[Sn^{IV}(TPP)(BF_4)_2]$ at room temperature (Scheme 1).

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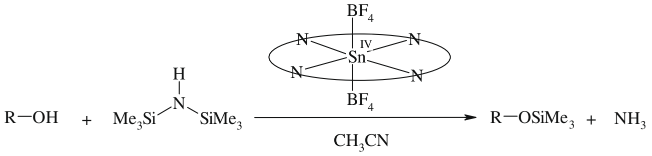


Scheme 1. Trimethylsilylation of alcohols and phenols with HMDS catalyzed by [$Sn^{IV}(TPP)(BF_4)_2$].

2. Experimental

Chemicals were purchased from Merck chemical company. ^1H NMR spectra were recorded in $CDCl_3$ solvent on a Bruker AM 80 MHz or a Bruker AC 400 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 20M columns and *n*-decane was used as internal standard. The tetraphenylporphyrin was prepared and metallated according to the literature [43,44]. The [$Sn^{IV}(TPP)(BF_4)_2$] catalyst was prepared as reported previously [40].

Table 1
Investigation of catalytic activity of different metalloporphyrin catalysts in the trimethylsilylation of 4-chlorobezyl alcohol with HMDS.[a]

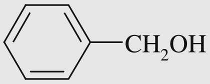
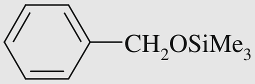
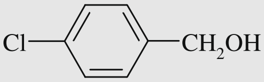
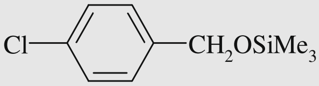
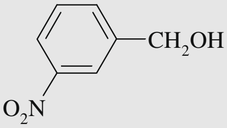
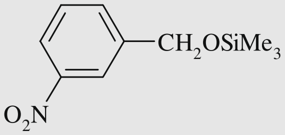
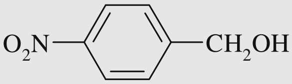
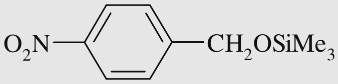
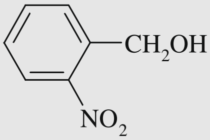
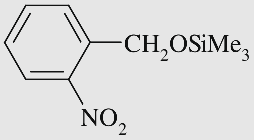
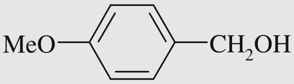
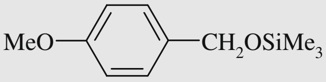
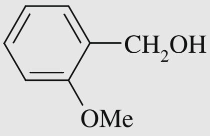
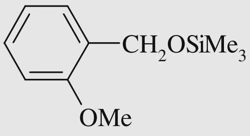
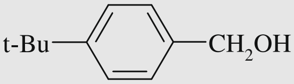
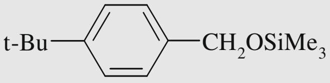
Entry	Catalyst	Time (min)	Yield (%)[b]
1	[$Sn^{IV}(TPP)(BF_4)_2$]	1	100
2	[SnIV(TPP)Cl_2]	1	21
3	[$Fe^{III}(TPP)(BF_4)$]	1	77
4	[$Mn^{III}(TPP)(BF_4)$]	1	43
5	[$Fe^{III}(TPP)Cl$]	1	26
6	[$Mn^{III}(TPP)Cl$]	1	17
7	[Cu(TPP)]	1	8

[a] Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), HMDS (0.5 mmol), catalyst (1 mol%), CH_3CN (0.5 ml).
[b] GC yield.

2.1. General procedure for the silylation of alcohols and phenols with HMDS catalyzed by [$Sn^{IV}(TPP)(BF_4)_2$]

A mixture of alcohol or phenol (1 mmol), [$Sn^{IV}(TPP)(BF_4)_2$] (10 mg, 0.01 mmol) and HMDS (0.5 mmol per OH group) in CH_3CN (1 mL) was prepared and stirred at room temperature for appropriate time (Table 1). The progress of the reaction was monitored by GC and TLC in 30 s intervals. After completion of the reaction, the

Table 2
Trimethylsilylation of alcohols with HMDS catalyzed by [$Sn^{IV}(TPP)(BF_4)_2$] at room temperature.[a]

Entry	Hydroxy compound	TMS-ether	Time (min)	Yield (%)[b]
1			1	100
2			1	100
3			2	100
4			2	100
5			2	100
6			1	100
7			2	100
8			1	100

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