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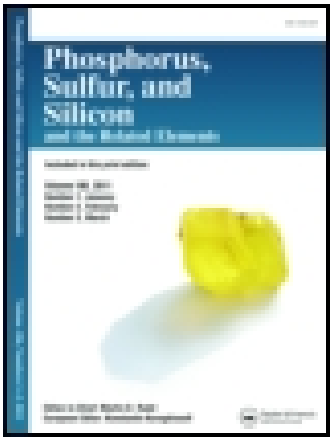

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HEXAMETHYLDISILAZANE IN THE PRESENCE OF N,N′,N″,N‴-TETRAMETHYLTETRA-2,3-PYRIDINOPORPHYRAZINATO COPPER (II) IS A NEW, MILD AND HIGHLY EFFICIENT REAGENT FOR SILYLATION OF ALCOHOLS AND PHENOLS

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HEXAMETHYLDISILAZANE IN THE PRESENCE OF N,N′,N″,N‴-TETRAMETHYLTETRA-2,3-PYRIDINOPORPHYRAZINATO COPPER (II) IS A NEW, MILD AND HIGHLY EFFICIENT REAGENT FOR SILYLATION OF ALCOHOLS AND PHENOLS

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Alcohols and phenols are protected with hexamethyldisilazane in the presence of N,N′,N″,N‴-tetramethyletra-2,3-pyridinoporphyrazinato copper (II) in good-to-excellent yields at room temperature.

Keywords: Alcohols; hexamethyldisilazane (HMDS); N,N′,N″,N‴,-tetramethyltetra-2,3-pyridinoporphyrazinato copper (II); phenols; silylation

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INTRODUCTION

The role of silyl groups has been recognized of late as an important part of organic chemistry from both analytical and synthetic points of view, especially as a protecting group in many syntheses of reasonable complexity.[1] Generally the formation of silyl ethers is carried out by treatment of alcohols with silyl chlorides or silyl triflates in the presence of a base,[2] Li_2S,[3] and sometimes a nonionic super base catalyst.[4] However, some of these methods frequently suffer from drawbacks such as lack of reactivity or the difficulty in removal of amine salts derived from the reaction of by-product acid and cobases during the silylation reaction. 1,1,1,3,3,3-Hexamethyldisilazane(HMDS) is a

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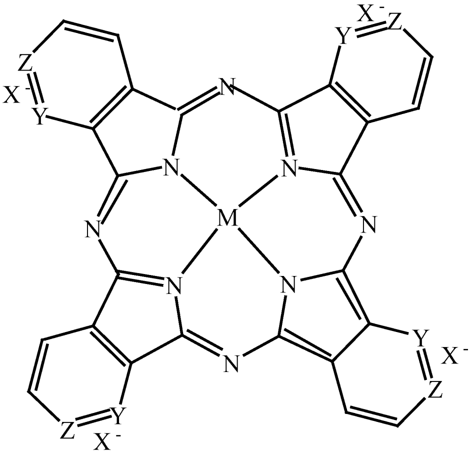
stable, commercially available, and cheap reagent for trimethylsilylation of hydrogen-labile substrates,[1a] giving ammonia as the only by-product. On the other hand, silylation using this silazan-type reagent is nearly neutral and does not need special precautions. However, the low silylating power of HMDS is a main drawback for its application, which needs forceful conditions and long reaction times in many instances. A variety of catalysts, such as $(CH_3)_3SiCl$,[5] $ZnCl_2$,[6] nitrogen ligand complexes of metalchlorides,[7] zirconium sulfophenyl phosphonate,[8] K-10 montmorilonite,[9] and special types of catalysts having the general formula X^1-NH-X^2 in which at least one of the groups X^1,X^2 is electron-withdrawing such as an ester or amide group, has also been reported for the silylation of a wide range of functional groups using HMDS.[10]

In this research we studied the catalytic effect of N,N′,N″,N‴,-tetramethyltetra-2,3-pyridinoporphyrazinato copper (II) ($[Cu(2,3\text{-}tmtppa)]^{4+}$) (I) in trimethylsilylation of alcohols and phenols (Figure 1).

The tetramethymetalloporphyrazine complexes are phthalocyanine derivatives in which the outer benzene rings are replaced with electron-withdrawing pyridine rings. Phthalocyanines closely resemble porphyrins in many of their physico-chemical properties.



$[Cu(2,3\text{-}tmtppa)]^{4+}$ (I)

Y= N^+-CH_3, Z= CH, X= CH_3SO_4

FIGURE 1

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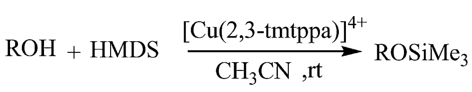
Two kinds of related compounds, namely the 2,3-pyridinoporphyrazine and 3,4-pyridinoporphyrazine, have been reported. The metal complexes of these compounds are synthesized by a template procedure analoguous to that of phthalocyanidine. The most common methods use dicyanopyridine or pyridinedicarboxylic acids. 2,3-pyridinoporphyrazine complexes are synthesized from 2,3-dicyanopyridine or 2,3-pyridinedicarboxlic acids. The synthetic methods for 3,4-pyridinoporphyrazines are essentially similar to those of the 2,3 congeners. The solubility of these complexes in common organic solvents is considerably low. The N,N′,N″,N‴-tetramethylated quaternized forms of tetrapyridinoporphyrazines are tetra-positively charged and hence water soluble. The water soluble form of mentioned complexes are prepared by quaternization of the pyridine nitrogen with dimethyl sulfate at 120°C in dimethyl formamid.[11,12]

Unlike phthalocyanines, the chemical and physical properties of tetrapyridinoporphyrazine complexes have received little attention. However, their uses as catalysts in thiol and cumen autoxidation have been described.[13,14]

RESULTS AND DISCUSSION

We are especially interested in exploring the potential use of neutral or nearly neutral catalyst. Herein, we wish to describe a new protocol for the mild and rapid trimethylsilylation of a wide variety of alcohols and phenols using HMDS and a catalytic amount of $[\mathrm{Cu(2,3\text{-}tmtppa)}]^{4+}$.

At first, the protection of benzyl alcohol under catalytic effect of $[\mathrm{Cu(2,3\text{-}tmtppa)}]^{4+}$ in acetonitrile at room temperature was studied. Benzyl trimethylsilyl ether was produced after 10 min in quantitative yield. We then applied these conditions for the protection of structurally different alcohols and phenols. (Scheme 1).



$$\mathrm{ROH} + \mathrm{HMDS} \xrightarrow[\mathrm{CH_3CN}\ ,\mathrm{rt}]{[\mathrm{Cu(2,3\text{-}tmtppa)}]^{4+}} \mathrm{ROSiMe_3}$$

R: primary, secondary , tertiary alkyl and phenyl

SCHEME 1

In order to optimize the reaction conditions, we first examined the effect of different ratios of ROH/DHP/catalyst. Employing the 1/0.8/0.01 ratio gave the best results and produced trimethylsilyl ethers in quantitative yields (Table I).

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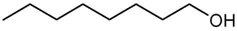
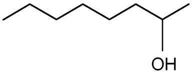
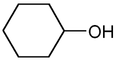
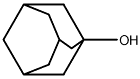
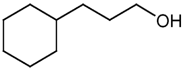
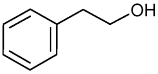
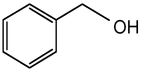
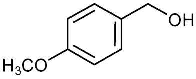
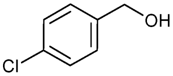
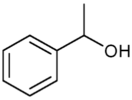
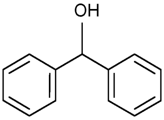
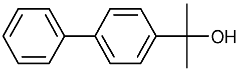
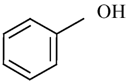
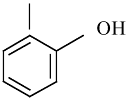
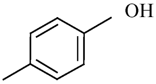
TABLE I Trimethylsilylation of Alcohols and Phenols Catalyzed by $[Cu(2,3tmtppa)]^{4+}$

Entry	ROH	Time (min)	Conversion (%)[a]	Isolated Yield (%)
1		10	100	92
2		15	100	90
3		20	100	93
4		4.5 (h)	100	85
5		5	100	98
6		5	100	96
7		5	100	98
8		5	100	97
9		5	100	91
11		20	100	93
12		30	100	95
13		4 (h)	100	95
14		3 (h)	100	93
15		3 (h)	100	90
16		75	100	94

[a] GC yield using internal standard.

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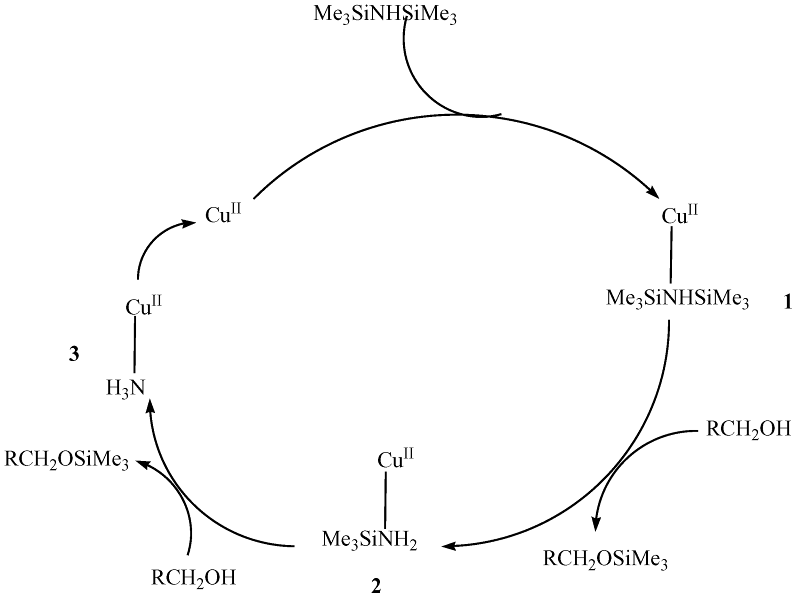
Compounds that were trimethylsilylated in this way are primary, secondary, tertiary, and benzylic alcohols. Generally, in the cases of primary and secondary alcohols the reactions were completed within less than 30 min in acetonitrile at room temperature accompanied by evolution of NH_3 gas from the reaction mixture.

The mechanism for these transformations is unclear. One idea may be that $[Cu(2,3\text{-tmtppa})]^{4+}$ acts as a Lewis acid, which may polarize the Si-N bond in HMDS to produce the silylating agent **1** (Scheme 2). A rapid reaction with alcohol then ensues, leading to **2** and the concomitant release of the corresponding silyl ether. This is followed by the formation of the ammonia-Cu^{II} complex **3**. Cleavage of **3** leads to the fast evolution of NH_3 and release of catalyst, which re-enters the catalytic cycle (Scheme 2). Nevertheless, at this time there is no experimental evidence for this feature of I, and the actual role of this reagent should be studied further in detail.



SCHEME 2

In this article we not only investigated one of the catalytic effect of $[Cu(tmtppa)]^{4+}$ in organic synthesis but also introduced an efficient solid acid catalyst for protection of hydroxyl groups with HMDS. This complex is an interesting catalyst with high reusable capacity and that separated from the reaction mixture easily. Also, workup and isolation of the product in this method is very easy.

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EXPERIMENTAL

The products were purified by column chromatography, and the purity determinations of the products were accomplished by GLC on a Shimadzu model GC-10A instrument or by TLC on silica-gel polygram STL G/UV 254 plates. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer RXI spectrometer. NMR Spectra were recorded on a Bruker Avance DPX 250 MHz instrument.

The catalyst was prepared and purified by the method described in the literature.[11]

Typical Procedure for the Protection of Benzyl Alcohol

To benzyl alcohol (1 mmol, 0.108 g) and HMDS (0.8 mmol, 0.128 g) in acetonitrile (5 ml), $[Cu(2,3\text{-tmtppa})]^{4+}$ (0.01 mmol, 0.0111 g) was added and the mixture stirred at room temperature. GC analysis showed that the reaction was completed after 5 min. The reaction mixture was filtered. Column chromatography of the filtrate on silica gel using n-hexane as eluent gave benzyl trimethylsilyl ether in 98% yield.

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