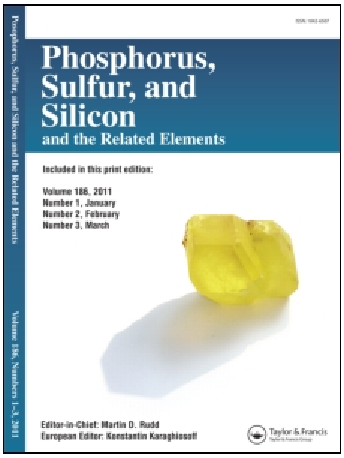

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Alumina Sulfuric Acid as an Efficient and Recyclable Heterogeneous Catalyst for the O-Silylation of Alcohols, Phenols, and Oximes

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Alumina sulfuric acid as a recyclable catalyst conducts the transformation of various types of alcohol, phenols, and oximes with hexamethyldisilazane (HMDS) to the corresponding O-trimethylsilylated compounds in good to excellent yields under mild and ambient conditions with short reaction times. The method is highly selective for the conversion of primary alcohols in the presence of secondary and tertiary alcohols. Additionally, the catalyst can be easily recovered and reused at least eight times without detectable loss of reactivity.

Keywords Alcohols; alumina sulfuric acid; hexamethyldisilazane; oximes; phenols; trimethylsilylation

INTRODUCTION

Trimethylsilylation of hydroxyl functional groups is frequently used as a protection method in several chemical transformations involving the multi-step synthesis of natural and synthetic products, and pharmaceuticals and is often used in analytical chemistry to prepare silyl ethers as volatiles derivatives of hydroxyl groups.[1] Silyl ethers are resistant to oxidation; have good heat stability; have low viscosity; and allow their parent compounds to be recovered easily.[2] Silyl ethers have a general stability for most non-acidic reagents, and a high solubility in non-polar solvents.[3]

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The preparation of silyl ethers can be carried out by treatment of alcohols with silyl chlorides or silyl triflates in the presence of a organic base.[7–14] However, some of these methods frequently suffered from drawbacks such as lack of reactivity or the difficulty in removal of amine salts.[4] 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is a stable, commercially available, and cost-effective reagent for trimethylsilylation of hydrogen-labile substrates, giving NH_3 as the only byproduct.[1–4] Even though the handling of this reagent is easy, the low silylating ability of HMDS is one of the main drawbacks to its continued application; therefore, there are a variety of catalysts for activating of this reagent, such as $(CH_3)_3SiCl$,[15] K-10 montmorillionite,[16] sulfonic acids,[17] zirconium sulfophenyl phosphonate,[18] $ZnCl_2$,[19] Envirocat EPZGO,[20] tungstophosphoric acid,[21] iodine,[22] lithium perchlorate,[23] cupric sulfate pentahydrate,[24] H–β Zeolite,[25] $MgBr_2$,[26] lithium perchlorate suported on silica gel,[27] $Al(HSO_4)_3$,[28] $Al(OTF)_3$,[29] magnesium triflate,[30] copper triflate,[31] $ZrCl_4$,[32] silica-$HClO_4$,[33] and silica chloride.[34]

However, in most of these cases, a long reaction time, drastic reaction conditions, or tedious workup is needed. In addition, many of these reagents are moisture sensitive or expensive. The lack of a facile and effective synthetic methodology for the silylation of hydroxyl groups prompted us to develop a convenient and practical procedure for the protection of hydroxyl groups in the presence of heterogeneous catalyst under ambient conditions. The use of heterogeneous catalysts is becoming very popular as it has many advantages: reduced pollution, reusability, high selectivity, low cost, and simplicity in process and in handling. These factors are especially important in industry. In the present research for functional group transformation, we wish to describe a new protocol for the mild and rapid trimethylsilylation of a wide variety of hydroxyl groups using HMDS and a catalytic amount of alumina sulfuric acid as a recyclable solid Brønsted acid catalyst at room temperature (Scheme 1).

$$\text{ROH} + \text{HMDS} \xrightarrow[\text{neat, r.t, } (\text{-NH}_3)]{\text{Alumina sulfuric acid (cat)}} \text{ROTMS}$$

time: 2 -150 min

R: Aryl, primary, secondary, tertiary alkyl, and oxime

SCHEME 1

This environmentally benign and inexpensive catalyst was prepared from the reaction of alumina with chlorosulfonic acid (Scheme 2).[35]

$$Al_2O_3 + ClSO_3H \longrightarrow Al_2O_3\text{-}SO_3H$$

SCHEME 2

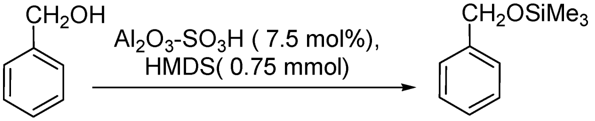
RESULTS AND DISCUSSION

To optimize the reaction conditions, initially, we tried to convert benzyl alcohol (1 mmol) to trimethylbenzyloxy silane with alumina sulfuric acid (0.025 g, 0.075 mmol of H^+)[35,36] and HMDS (0.75 mmol) in the presence of various solvents and also under solvent-free conditions (Table I).

As shown in Table I, the yield of the product in acetonitrile as a solvent is higher and the reaction time is shorter. Therefore, we employed the acetonitrile for the conversion of the various hydroxyl groups to the corresponding trimethylsilyl ethers (Scheme 1 and Table II).

A wide range of structurally diverse and functionalized alcohols, phenols and naphthols underwent silylation by this procedure provide the corresponding TMS ethers in good to excellent isolated yields (Table II, entries 1−23). Inspection of the data in Table II clearly shows that different types of hindered secondary and tertiary alcohols were successfully converted to the corresponding silyl ethers. Timethylsilylation of aldoxime and ketoxime also produce the corresponding trimethylsilyl ether at the same experimental conditions (Table II, Entries 24−26). In the all cases, the desired trimethylsilyl ethers were prepared accompanied by evolution of NH_3 gas from the reaction mixture.

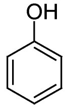
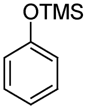
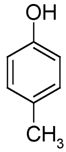
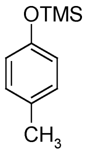
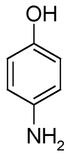
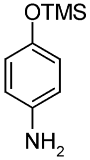
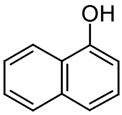
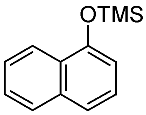
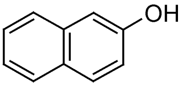
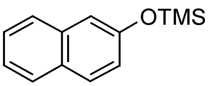
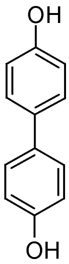
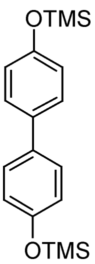
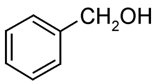
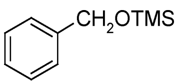
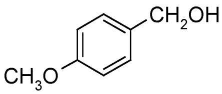
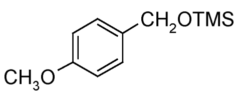
TABLE I Trimethyl Silylation of Benzyl Alcohols (1 mmol) with HMDS (0.75) in the Presence of Alumina Sulfuric Acid as Catalyst under Ambient Conditions



Entry	Solvent	Time (min)	GC Yield (%)	Yield (%)[a]
1	Dichloromethane	25	100	89
2	Chloroform	20	100	91
3	Ethyl acetate	70	100	91
4	n-Hexane	60	100	93
5	Diethyl ether	40	100	89
6	Acetonitrile	2	100	98
7	Solvent-Free	75	100	93

[a] Yields refer to pure isolated trimethylbenzyloxy silane.

TABLE II Silylation of Alcohols, Phenols, Naphthols, and Oximes (1 mmol) with HMDS (0.75 mmol) in the Presence of Alumina Sulfuric Acid as Catalyst (0.025 g, 7.5 mol% of H$^+$) in Acetonitrile under Ambient Conditions

Entry	Substrate	Product	Sub/ HMDS ratio	Time (min)	Yield[a] (%)
1			1/0.75	4	96–98[b]
2			1/0.75	4	96
3			1/1.4	5	91
4			1/0.75	3	96
5			1/0.75	4	95
6			1/1.5	3	95
7			1/0.75	2	98
8			1/0.75	2	95

(Continued on next page)

TABLE II Silylation of Alcohols, Phenols, Naphthols, and Oximes (1 mmol) with HMDS (0.75 mmol) in the Presence of Alumina Sulfuric Acid as Catalyst (0.025 g, 7.5 mol% of H$^+$) in Acetonitrile under Ambient Conditions (Continued)

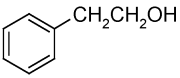
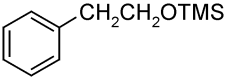
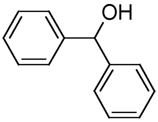
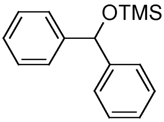
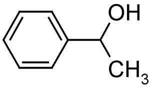
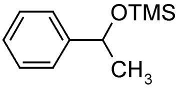
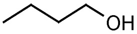
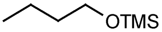
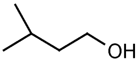
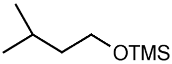
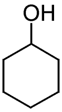
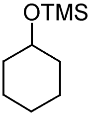
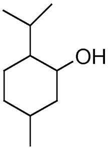
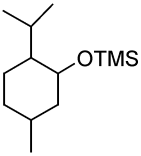
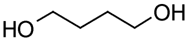
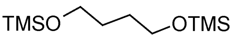
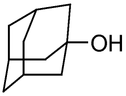
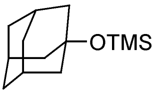
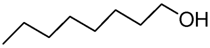
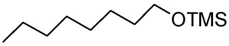
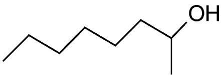
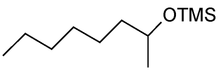
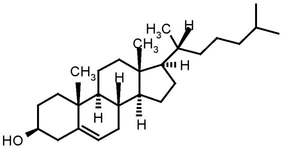
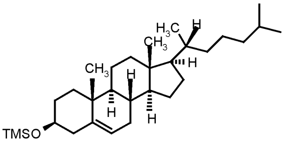
Entry	Substrate	Product	Sub/ HMDS ratio	Time (min)	Yield^a (%)
9			1/0.75	12	97
10			1/0.75	7	89
11			1/0.75	8	91
12			1/0.75	10	85
13			1/0.75	8	87
14			1/0.75	15	91
15			1/0.75	13	95
16			1/1.35	8	90
17			1/0.75	150	95
18			1/0.75	7	95
19			1/0.75	12	93
20			1/0.75	6	97

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TABLE II Silylation of Alcohols, Phenols, Naphthols, and Oximes (1 mmol) with HMDS (0.75 mmol) in the Presence of Alumina Sulfuric Acid as Catalyst (0.025 g, 7.5 mol% of H$^+$) in Acetonitrile under Ambient Conditions (Continued)

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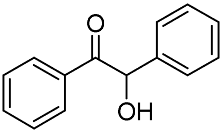
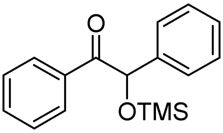
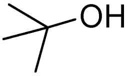
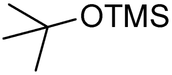
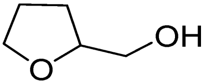
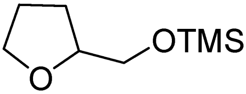
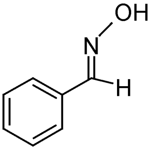
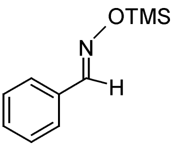
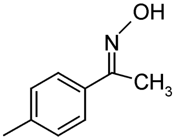
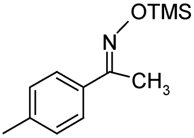
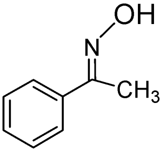
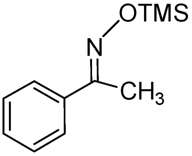
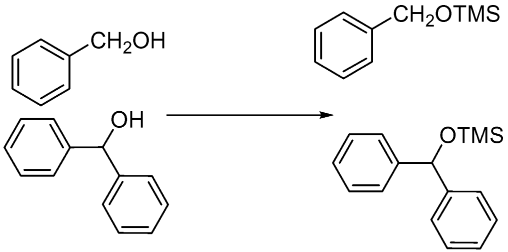
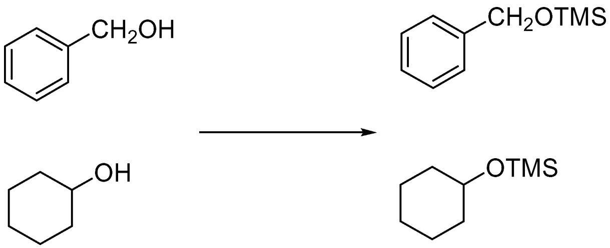
21			1/0.75	15	89
22			1/0.75	65	86
23			1/0.75	7	94
24			1/0.75	7	90
25			1/0.75	8	89
26			1/0.75	8	92

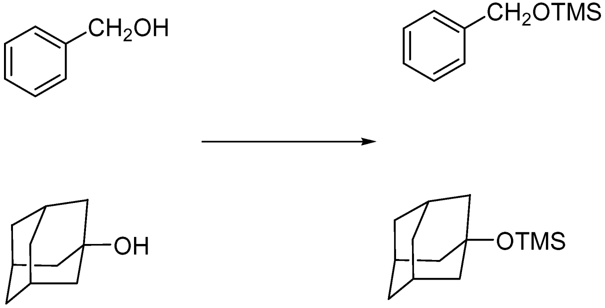
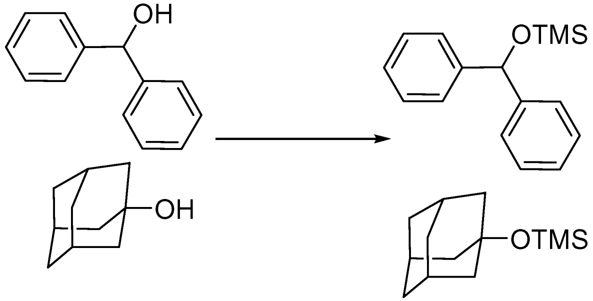
[a] Yields refer to the pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of IR and NMR spectra with authentic samples.[15–34]

[b] The yields of eight consecutive catalytic reactions using the recovered catalyst.

We also investigated selective silylation of different binary mixture of alcohols in Table III. This method was shown highly selectivity for primary alcohols such as benzyl alcohols (Table III, entries 1–3). The primary alcohols were completely converted to the corresponding silylethers, while only 15–21% conversion was observed for the secondary alcohols (Table III, entries 1, 2). Excellent selectivity was

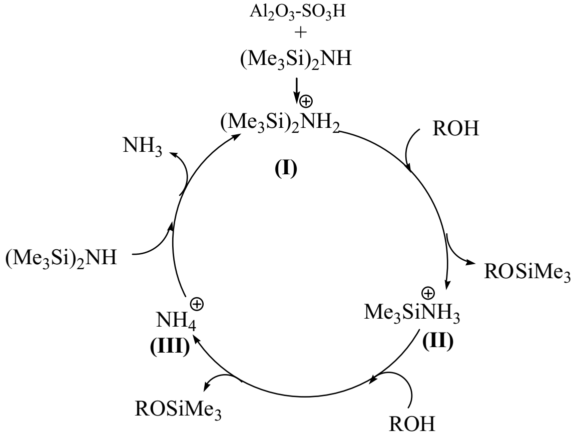
TABLE III Selective Silylation of Different Binary Mixture of Alcohols

Entry	Substrate product binary mixture	Molar ratio sub1/sub2/HMDS/catalyst	Time (min)	GC yield (%)
1		1/1/0.7/ 0.075	40	100 15
2		1/1/0.7/0.075	5	100 21

3		1/1/0.7/0.075	5	100 0
4		1/1/0.7/0.075	32	100 8

also observed for the conversion of primary and secondary alcohols in the presence of tertiary alcohols such as adamantanol (Table III, entries 3, 4).

The suggested mechanism of the alumina sulfuric acid catalyzed transformation is shown in Scheme 2. We suggested this mechanism according to the evolution of NH_3 under the reaction conditions. We propose that an acid-base interaction between H^+ in alumina sulfuric acid as catalyst and nitrogen in HMDS polarizes N-Si bond of HMDS to produce a reactive silylating agent (**I**). A rapid reaction with alcohol then ensues, leading to the ammonium silylating species (**II**) with concomitant release of the corresponding silyl ether. Irreversible cleavage of (**II**) with alcohol leading to ROTMS and also formation of NH_4^+. Release of H^+ from intermediate (**III**), leading to the fast evolution of NH_3 and re-enters catalytic cycle (Scheme 3).

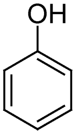
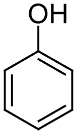
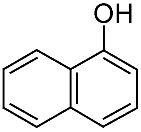
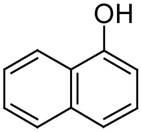
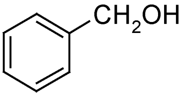
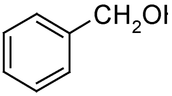


SCHEME 3

To show the efficiency of the non toxic alumina sulfuric acid in comparison with reported results in the literature, Table IV compares some of our results with iodine,[22] lithium perchlorate,[23] and cupric sulfate pentahydrate[24] respect to reaction times, easy work up and yields of the obtained products.

The catalyst could be separated by filtering it from the reaction mixture and then washing with ethyl acetate followed by draying in an oven at 100°C for 30 min. The reusability of the recovered catalyst was checked by the reaction of benzyl alcohol and HMDS in the presence of the 7.5 mol% of Al_2O_3-SO_3H at ambient conditions (Table II,

TABLE IV Comparison Result of Alumina Sulfuric Acid with Iodine[22] Lithium Perchlorate,[23]and Cupric Sulfate Pentahydrate[24] in the Synthesis of Trimethylsilyl Ethers Using HMDS

Entry	Substrate	Product	Subs/HMDS/ Catalyst	Condition	Yield[e] (%)
1			a) 1/0.8/0.01	CH_2Cl_2 as solvent; r.t.	–[a]
			b) 1/0.7/0.5	Solvent-free; r.t.; time= 20 min	96[b]
			c) 1/0.7/0.01	CH_3CN as solvent; r.t.; time = 1.5 h	95[c]
			d) 1/0.75/0.075	CH_3CN as solvent; r.t. ; time = 4 min	97[d]
2			a) 1/0.8/0.01	CH_2Cl_2 as solvent; r.t.	–[a]
			b) 1/0.7/0.5	Solvent-free; r.t.; time= 20 min	80[b]
			c) 1/0.7/0. 1	CH_3CN as solvent; r.t.; time = 38 h	50[c]
			d) 1/0.75/0.075	CH_3CN as solvent; r.t.; time = 4 min	96[d]
3			a) 1/0.8/0.01	CH_2Cl_2 as solvent; r.t.; time = 2 min	98[a]
			b) 1/0.7/0.5	Solvent-free; r.t.; time= 25 min	99[b]
			c) 1/0.7/0. 01	CH_3CN as solvent; r.t.; time = 12 min	98[c]
			d) 1/0.75/0.075	CH_3CN as solvent; r.t.; time = 2 min	98[d]

Catalyst: [a]iodine; [b]lithium perchlorate; [c]cupric sulfate pentahydrate; [d]alumina sulfuric acid; and [e]isolated yield.

entry 1). The results indicate that the recovered catalyst can be used at least eight consecutive times without any loss of its activity.

In conclusion, we have demonstrated that alumina sulfuric acid is a new, efficient and heterogeneous catalyst for trimethylsilylation of a variety of hydroxyl groups using HMDS under ambient conditions. The reactions were carried out at room temperature with short reaction time and produce the corresponding timethylsilyl ethers in good to excellent yields. Reusability of the recovered catalyst, simple work-up procedure, including filtering the mixture through a short pad of silica gel column followed by evaporation of the solvent, is another advantage of this method.

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and used without further purification. Alumina sulfuric acid was prepared according to the reported procedure.[35,36] All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopy data (IR, ^{1}H NMR spectra). The NMR spectra were recorded on a Bruker Avance DPX 300 and 500 MHz instrument. The spectra were measured in $CDCl_3$ relative to TMS (0.00 ppm). GC analysis was run with Shimadzu GC-14A. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. TLC was performed on Silica-gel polygram SIL G/UV 254 plates.

General Procedure for Silylation of Alcohols Using HMDS Catalyzed with Al_2O_3-SO_3H

To a stirred solution of alcohol (1 mmol) and HMDS (0.75 mmol) was added alumina sulfuric acid (0.025 g, 0.075 mmol of H^+) and the mixture was stirred at room temperature for the time specified in Table II. The reaction was followed by TLC (n-Hexane-EtOAc, 9:1). After completion of the reaction, the heterogeneous catalyst was filtered and the resulting mixture was passed through a short pad of silica gel. Then, the pad column was washed with n-hexane (2 × 10 mL). Evaporation of the solvent under reduced pressure gave pure product(s) (Table II). The desired pure product(s) was characterized by comparison of their physical data with those of known compounds.[15–34]

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