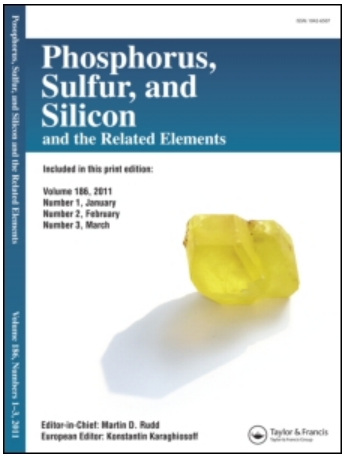

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$Al(HSO_4)_3$ as an Efficient Reagent for the Selective Trimethylsilylation of Primary Alcohols Under Solvent-Free Conditions

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Primary alcohols are selectively trimethylsilylated using Hexamethyldisilazane (HMDS) in the presence of a catalytic amount of $Al(HSO_4)_3$ under solvent free conditions.

Keywords Alcohols; $Al(HSO_4)_3$; hexamethyldisilazane (HMDS); solvent-free conditions; trimethylsilylation

Trimethylsilylation is one of the important methods that is used for the protection of the hydroxyl group.[1] A large number of reagents and methods have been reported for this purpose, such as allylsilanes,[2,3] chlorotrimethylsilane/lithium disulfate,[4] hexamethyldisiloxane,[5] and N-trimethyl-2-oxazolidinone.[6]

Hexamethyldisilazane (HMDS) is a stable, commercially available, and cheap reagent for trimethylsilylation of hydrogen-labile substrates,[1] giving ammonia as the only byproduct. On the other hand, silylation using this 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

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reaction times in many instances. A variety of catalysts such as zirconium sulfophenyl phosphonate,[7] K-10 montmorilonite,[8] Me_3SiCl,[9] sulfonic acids,[10] and nitrogen ligand complexes of methachlorides[11] have been reported for the activation of HMDS.

Solvent-free reactions have attracted considerable attention in chemical processes for different reasons. They are valuable due to environmental safety, the economic viewpoint, easy work up, high yields of the products, and (usually) their fast reactions.[12]

In continuation of our studies on the applications of $Al(HSO_4)_3$,[13–16] herein we wish to report a mild and efficient method for the trimethylsilylation of primary alcohols using HMDS in the presence of a catalytic amount of this reagent (Scheme 1). All reactions were performed at 80°C under solvent-free conditions in good to high yields.

$$RCH_2OH \xrightarrow[\text{Solvent free, } 80^\circ C]{\text{HMDS, } Al(HSO_4)_3} RCH_2OSiMe_3$$

SCHEME 1

As shown in Table I, trimethylsilylation of the secondary and tertiary alcohols using this method is very slow (Table I, entries 12–15). Therefore, this methodology can be used for the selective silylation between primary and secondary or tertiary alcohols. This is exemplified by the competitive reaction between 4-chlorobenzylalcohol and triphenylmethanol (Table I, entry 16).

In order to show the efficiency of this method, we have compared some of the results with some of those reported in the literature (Table II).[17,18]

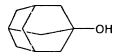
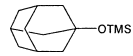
The mildness of the reaction conditions, high efficiency, selectivity, reasonable yields of products, a simple and clean work up, and solvent-free reaction conditions are among the advantages of this new method.

EXPERIMENTAL

General

Chemicals were purchased from Fluka, Merck, and Aldrich. Products were separated and purified by different chromatographic techniques and were identified by the comparison of their m.p., IR, NMR, and refractive index with those reported for the authentic samples. All yields refer to the isolated products. The purity determination of the substrates and reaction monitoring were accompanied by TLC on silica gel polygram SILG/UV 254 plates. Column chromatography was carried out on Merck kisselgel 60H.

TABLE I Selective Trimethylsilylation of Alcohols Under Solvent-Free Conditions[a]

Entry	Substrate	Product	Time (h)	Yield %[b]
1	2-$ClC_6H_4CH_2OH$	2-$ClC_6H_4CH_2OTMS$	0.42	92
2	4-$ClC_6H_4CH_2OH$	4-$ClC_6H_4CH_2OTMS$	0.08	90
3	2-$BrC_6H_4CH_2OH$	2-$BrC_6H_4CH_2OTMS$	0.42	90
4	4-$Me_3CC_6H_4CH_2OH$	4-$Me_3CC_6H_4CH_2OTMS$	0.33	90
5	2-$MeC_6H_4CH_2OH$	2-$MeC_6H_4CH_2OTMS$	0.25	95
6	2-$O_2NC_6H_4CH_2OH$	2-$O_2NC_6H_4CH_2OTMS$	0.75	92
7	4-$O_2NC_6H_4CH_2OH$	4-$O_2NC_6H_4CH_2OTMS$	0.33	90
8	$PhCH_2CH_2OH$	$PhCH_2CH_2OTMS$	0.42	90
9	PhCH(Me)CH_2OH	PhCH(Me)CH_2OTMS	1.12	80
10	$PhCH_2CH_2CH_2OH$	$PhCH_2CH_2CH_2OTMS$	0.33	85
11	$PhCH{=}CHCH_2OH$	$PhCH{=}CHCH_2OTMS$	0.33	90
12	Ph_2CHOH	$Ph_2CHOTMS$	4	50
13			4	50
14			2.5	50
15	Ph_3COH	$Ph_3CHOTMS$	4.5	5
16	4-$ClC_6H_4CH_2OH$ + Ph_3COH	4-$ClC_6H_4CH_2OTMS$ + $Ph_3CHOTMS$	0.08	85[c] + 0[c]

[a]Products were identified spectroscopically and also by the conversion of the products to their corresponding alcohols.

[b]Isolated yield.

[c]GC yield.

General Procedure for Trimethylsilylation of Primary Alcohols Under Solvent-Free Conditions

HMDS (0.75 mmol), alcohol (1 mmol) and $Al(HSO_4)_3$ (0.06 mmol, 0.02 g) were mixed and heated in an oil bath (80°C) for the specified time (Table I). After completion of the reaction (monitored by TLC or GC),

TABLE II Comparison of Some of the Results That Were Obtained by the Silylation of Alcohols with HMDS in the Presence of $Al(HSO_4)_3$(1), With Some of Those reported by $LiClO_4$ (2),[17] and Silica Chloride (3)[18]

		(min) (Yield %) (Substrate: HMDS: Catalyst)		
Entry	Substrate	1	2	3
1	2-Methylbenzyl alcohol	(15) (95)	—	(36) (90)
2	4-Chlorobenzyl alcohol	(4.8) (92)	(1.8) (67)	(30) (92)
3	Cinnamyl alcohol	(20) (90)	(1) (70)	(18) (70)

n-hexane (5 mL) was added and then filtered. The solid residue was washed with n-hexane (20 mL). The filtrate was then washed with water (10 mL) to destroy the extra amounts of HMDS and the organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the highly pure product. Further purification proceeded by bulb-to-bulb distillation under reduced pressure, vacuum distillation, or recrystallization to afford pure silyl ether.

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