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The Use of Silica Sulfuric Acid as an Efficient Catalyst for Deprotection of Trimethylsilyl Ethers to the Corresponding Alcohols under Mild and Heterogeneous Conditions

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Silica sulfuric acid was used as a suitable catalyst for the conversion of trimethylsilyl ethers to the corresponding alcohols in the presence of wet SiO_2 in high yields at room temperature.

Keywords: Silica sulfuric acid, Trimethylsilyl ethers, Alcohols

INTRODUCTION

Protection and deprotection of functional groups are important processes in organic synthesis [1]. Silyl protecting groups have played increasingly important roles in the synthesis of complicated molecules, especially for the synthesis of biologically significant products [2]. Although there have been many new reports of protection and deprotection of silyl groups, the removal of silyl group under mild conditions with an easy workup procedure is of preimary importance [3].

The development of environmentally benign technologies is the most challenging goal of contemporary chemistry and chemical engineering. Environmentally friendly chemical processes should be designed to use environmentally benign feeds and solvents, and utilize efficient reagent or catalyst recyclable systems. In the development of industrial processes, separation is very important. Efficient separation of reagents and catalysts to enable their reuse for subsequent reaction cycles are also key challenges. Especially in the stream of green chemistry, separation protocols that allow for the effective recovery of reagents and catalysts have been increasingly appreciated [4].

Acids are widely used as catalysts in industry, producing more than 1×10^8 mt of products/year. The most commonly used acids are HF, H_2SO_4, $HClO_4$, and H_3PO_4 (in liquid form or supported on Kieselguhr). Solid acids have many advantages such as simplicity in handling, fewer reactor and plant corrosion problems and environmentally safe disposal [5].

On the other hand, any reduction in the amount of sulfuric acid needed and/or any simplification in handling procedures is required for risk reduction, economic advantage and environmental protection [6]. In addition, current research and general interest in heterogeneous systems is due to their importance in industry and in developing technologies [7].

Among reported solid acids, silica sulfuric acid [8] has been used to catalyze a wide variety of reactions ranging from

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aldol condensation [9], acetalization [10], deacetalization [11], oxidation of alcohols [12], N-nitrosation of secondary amines [13], direct etherification of trimethylsilylethers [14] and so forth. Therefore, we decided to apply this catalyst to the conversion of trimethylsilyl ethers to their corresponding alcohols in the presence of wet SiO_2 at room temperature.

EXPERIMENTAL

Chemicals

Chemicals were purchased from Fluka, Merck, and Aldrich chemicals companies.

The products were characterized by comparison of their spectral (IR, ^{1}H NMR), TLC, and physical data with the standard samples. All silyl ethers were synthesized as previously published [16].

General Procedure

A mixture of the substrate 1 (1 mmol; see Table 1 for substrates and stirring times), n-hexane (5 ml), silica sulfuric acid (0.05 g), and wet SiO_2 (0.2 g) was stirred at room temperature for the specified time. The reaction was monitored by TLC using a 1:1 mixture of ether-petroleum ether as an eluent. After completion of the reaction the mixture was filtered and the solid residue was washed with n-hexane. Evaporation of the solvent gave pure alcohols in good to excellent yields (85-96%, Table 1).

RESULTS AND DISCUSSION

In this work, silica sulfuric acid was successfully used as a suitable catalyst for the conversion of several trimethylsilyl ethers to their corresponding alcohols in the presence of wet SiO_2 in high yields at room temperature, as shown in Scheme 1.

The direct conversion of 21 different trimethylsilylethers to the corresponding alcohols was carried out in the presence of silica sulfuric acid and wet SiO_2 in n-hexane at room temperature, based on the general procedure given in the Experimental section. The results are summarized in Table 1. As shown in Table 1, all corresponding alcohols were obtained at high yields (85-96%) in relatively short periods of time (12-40 min).

$$\mathrm{ROTMS} \xrightarrow[\text{Wet SiO}_2\text{, n-Hexane, r.t.}]{\text{Silica Sulfuric Acid}} \mathrm{ROH}$$

Scheme 1

We believe that the presence of wet SiO_2 provides an effective surface area for *in situ* generation of H_2SO_4. The reaction is clean and the purification of product is straightforward.

In conclusion, silica sulfuric acid was found to act as an excellent, easy to use, inexpensive, insoluble proton source in all organic solvents. The low cost and availability of the reagents, easy procedure and work-up make this method attractive for large scale operations. At the same time, silica sulfuric acid can serve as an efficient catalyst for the conversion of trimethylsilyl ethers into their corresponding alcohols under mild and heterogeneous conditions. The yields are good to excellent and the procedure is simple and convenient. In addition, silica sulfuric acid can be reused several times. Moreover, the reaction is heterogeneous and may be useful industrially [15].

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Table 1. Direct Conversion of Trimethylsilylethers **1** to the Corresponding Alcohols **2** in the Presence of Silica Sulfuric Acid[a]

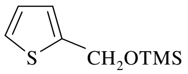
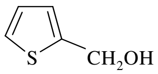
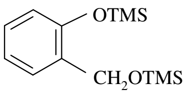
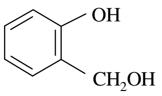
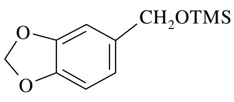
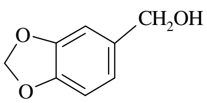
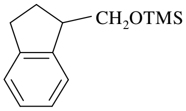
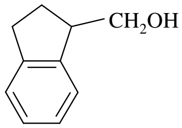
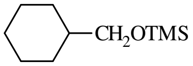
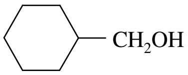
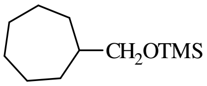
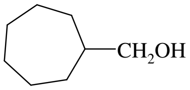
Entry	Substrate	1	Product	2	Time (min)	Yield (%)
1	4-$CH_3OC_6H_4CH_2OTMS$	**a**	4-$CH_3OC_6H_4CH_2OH$	**a**	12	95
2	$C_6H_5CH(OTMS)CH_2OTMS$	**b**	$C_6H_5CH(OH)CH_2OH$	**b**	25	94
3	4-$(CH_3)_2CHC_6H_4CH_2OTMS$	**c**	4-$(CH_3)_2CHC_6H_4CH_2OH$	**c**	18	96
4	4-$(CH_3)_3CC_6H_4CH_2OTMS$	**d**	4-$(CH_3)_3CC_6H_4CH_2OH$	**d**	18	95
5	2-$ClC_6H_4CH_2OTMS$	**e**	2-$ClC_6H_4CH_2OH$	**e**	35	92
6	4-$ClC_6H_4CH_2OTMS$	**f**	4-$ClC_6H_4CH_2OH$	**f**	25	94
7	2,4-$Cl_2C_6H_3CH_2OTMS$	**g**	2,4-$Cl_2C_6H_3CH_2OH$	**g**	40	91
8	2-$BrC_6H_4CH_2OTMS$	**h**	2-$BrC_6H_4CH_2OH$	**h**	35	90
9	2-$O_2NC_6H_4CH_2OTMS$	**i**	2-$O_2NC_6H_4CH_2OH$	**i**	38	91
10	3-$O_2NC_6H_4CH_2OTMS$	**j**	3-$O_2NC_6H_4CH_2OH$	**j**	39	89
11	4-$O_2NC_6H_4CH_2OTMS$	**k**	4-$O_2NC_6H_4CH_2OH$	**k**	26	94
12	$C_6H_5CH(CH_3)CH_2OTMS$	**l**	$C_6H_5CH(CH_3)CH_2$ OH	**l**	25	96
13	$C_6H_5CH{=}CHCH_2OTMS$	**m**	$C_6H_5CH{=}CHCH_2OH$	**m**	23	93
14	n-$C_7H_{15}OTMS$	**n**	n-$C_7H_{15}OH$	**n**	19	90
15	n-$C_8H_{17}OTMS$	**o**	n-$C_8H_{17}OH$	**o**	20	91
16		**p**		**p**	40	89
17		**q**		**q**	24	94
18		**r**		**r**	25	90
19		**s**		**s**	27	88

Table 1. Continued

20		**t**		**t**	18	88
21		**u**		**u**	20	85

[a]All amounts of reagents are listed in the Experimental section except in entries 2 and 17 the amounts of reagent and wet SiO_2 are 0.1 g.

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