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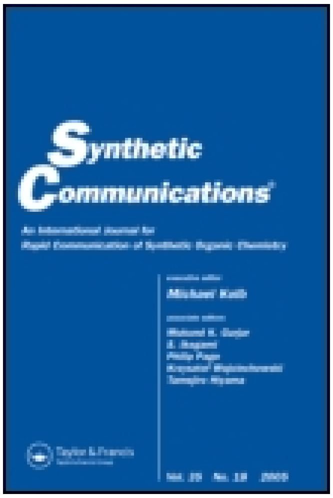

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High-Efficiency Conversion of Trimethylsilyl Ethers to Their Corresponding Ethers using Carbon-Based Solid Acid as a New Catalyst in Heterogeneous Mixtures

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High-Efficiency Conversion of Trimethylsilyl Ethers to Their Corresponding Ethers using Carbon-Based Solid Acid as a New Catalyst in Heterogeneous Mixtures

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Abstract: Carbon-based solid acid was used as a new catalyst for conversion of trimethylsilyl ethers to their corresponding ethers in heterogeneous mixtures. The experiments were done moderately at room temperature, and high yields in suitable times were obtained under these conditions.

Keywords: carbon-based solid acid, heterogeneous mixtures, trimethylsilyl ether

INTRODUCTION

Sulfuric acid is an essential catalyst for the production of industrial chemicals. However, such liquid-acid catalyst requires special processing in the form of neutralization, which involves costly and inefficient separation of catalyst from product and results in an unrecyclable sulfate waste.

According the principal of green chemistry, the production method should be refined so as to minimize adverse effect on the environment and human health.[1] The migration to strong acids, which are recyclable and nontoxic, from liquid acids such as sulfuric acid is therefore a desirable

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goal.[2,3] Solid acids are conventional materials that have wide applications in chemical production, separation/purification, and polymer–electrolyte fuel-cell (PEFC) technologies, and the chemical industry is currently searching for a highly active and stable solid acid to improve the environmental safety of the production of chemicals and energy. An ideal solid material for the applications considered here should have high stability and numerous strong protonic acid sites.[4] Michikazu Hara and coworkers, reported the synthesis of a carbon-based solid acid with a high density of sulfonic acid groups (SO_3H). Such carbon-based solid acids can be readily prepared by heating aromatic compounds such as naphthalene in sulfuric acid at 473–573 K.[5] In this synthesis, the sulfonation of the aromatic compounds is the first stage of the reaction. The resulting sulfonated aromatic compounds are incompletely carbonized, which results in the formation of a solid with a nominal sample composition of $CH_{0.35}\ O_{0.35}S_{0.14}$. The resulting black powder is insoluble in solvents such as water, methanol, ethanol, benzene, and hexane, even at boiling temperatures.

Symmetrical and unsymmetrical alkyl/aryl ether formation is an important reaction in organic synthesis and has generated significant interest in recent years.[6–10] The classic Williamson procedure, the Mitsunobu reaction, and the Ullmann condensation method can be use for this transformation. Ion-exchange resin and heteroploy acid–catalyzed etherification have also been reported.[11–14] Rearrangement and elimination of alkyl alcohols that are sterically hindered is the major disadvantage of the older procedures for ether synthesis. This problem is amplified when the alcohols are immobilized on solid supports and the activated species becomes the limiting reagent.[15] The alcohol–sulfuric acid reaction is most often used for the conversion of simple primary alcohols into symmetrical ethers. Secondary and tertiary alcohols predominantly undergo dehydration when subjected to these conditions. Occasionally a small amount of the symmetrical ether is formed as a by-product in the case of secondary alcohols.[16] In 1987, Sassaman's group reported a facile procedure for the synthesis of symmetrical and unsymmetrical ethers via reductive coupling of carbonyl compounds under mild acid-free conditions.[17]

The goal of this work is conversion of trimethylsilyl ether to the corresponding ether in the presence of a carbon-based solid acid. In the proposed procedure, this reagent was used for ether synthesis from primary and secondary trimethylsilyl ether (Scheme 1).

$$\underset{\mathbf{1}}{\mathrm{RR'HCOTMS}} \xrightarrow[\text{n-Hexane, rt.}]{\text{Carbon-based solid acid}} \underset{\mathbf{2}}{\mathrm{(RR'HC)_2O}}$$

Scheme 1.

EXPERIMENTAL

General

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The products were characterized by comparison of their spectral (IR, ^1H NMR), thin-layer chromatographic (TLC), and physical data with the authentic samples. All silyl ethers were synthesized according to the reported procedure.[18]

Typical Experimental Procedure

A mixture of the substrate **1** (4 mmol), *n*-hexane (20 mL), and carbon-based solid acid (0.8 g) was stirred at room temperature for the specified time. The trimethylsilyl compounds, the corresponding ether products, time of reaction, and percentage of yield of reactions are collected in Table 1.

Table 1. Direct conversion of primary and secondary trimethylsilyl ethers to corresponding ethers on the carbon-based solid acid as catalyst

Entry	Substrates	Products[a]	Time (min)	Yield (%)
1	$2\text{-}CH_3OC_6H_4CH_2OTMS$	$(2\text{-}CH_3OC_6H_4CH_2)_2O$	7	85
2	$3\text{-}CH_3OC_6H_4CH_2OTMS$	$(3\text{-}CH_3OC_6H_4CH_2)_2O$	7	90
3	$4\text{-}CH_3OC_6H_4CH_2OTMS$	$(4\text{-}CH_3OC_6H_4CH_2)_2O$	7	90
4	$4\text{-}(CH_3)_2CHC_6H_4CH_2OTMS$	$(4\text{-}(CH_3)_2CH\ C_6H_4CH_2)_2O$	7	90
5	$4\text{-}(CH_3)_3CC_6H_4CH_2OTMS$	$(4\text{-}(CH_3)_3C\ C_6H_4CH_2)_2O$	7	90
6	$2\text{-}ClC_6H_4CH_2OTMS$	$(2\text{-}ClC_6H_4CH_2)_2O$	20	85
7	$4\text{-}ClC_6H_4CH_2OTMS$	$(4\text{-}ClC_6H_4CH_2)_2O$	21	85
8	$2,4\text{-}Cl_2C_6H_3CH_2OTMS$	$(2,4\text{-}Cl_2C_6H_3CH_2)_2O$	28	80
9	$2\text{-}BrC_6H_4CH_2OTMS$	$(2\text{-}BrC_6H_4CH_2)_2O$	28	85
10	$2\text{-}O_2NC_6H_4CH_2OTMS$	$(2\text{-}O_2NC_6H_4CH_2)_2O$	20	85
11	$3\text{-}O_2NC_6H_4CH_2OTMS$	$(3\text{-}O_2NC_6H_4CH_2)_2O$	27	80
12	$4\text{-}O_2NC_6H_4CH_2OTMS$	$(4\text{-}O_2NC_6H_4CH_2)_2O$	28	90
13	$C_6H_5CHCH_3CH_2OTMS$	$(C_6H_5CHCH_3CH_2)_2O$	8	85
14	$C_6H_5CH{=}CHCH_2OTMS$	$(C_6H_5CH{=}CHCH_2)_2O$	7	80
15	$4\text{-}C_6H_5CH_2OC_6H_4CH_2OTMS$	$(4\text{-}C_6H_5CH_2OC_6H_4CH_2)_2O$	7	80
16	$n\text{-}C_7H_{15}OTMS$	$(n\text{-}C_7H_{15})_2O$	7	80
17	$n\text{-}C_8H_{17}OTMS$	$(n\text{-}C_8H_{17})_2O$	8	80
18	$(C_6H_5)_2CHOTMS$	$((C_6H_5)_2CH)_2O$	20	85
19	$4\text{-}ClC_6H_4CHCH_3OTMS$	$(4\text{-}ClC_6H_4CHCH_3)_2O$	32	85
20	$C_6H_5CH_3CHOTMS$	$(C_6H_5CH_3CH)_2O$	14	80

[a] All of the products are known and their spectral and other data match those reported in the literature.

All of the products are known, and their spectral and physical data match those reported in the literature. The percentages of yield are isolated yields. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the solid residue was washed with *n*-hexane solvent. Evaporation of the solvent was followed by column chromatography on silica gel, and pure ether was obtained in excellent yields. In conclusion, carbon-based solid acid can serve as an efficient catalyst for the direct conversion of primary and secondary trimethylsilyl ethers into the corresponding ethers under mild and heterogeneous conditions in a short period of time. The yields are excellent, and the procedure is simple and convenient. Rearrangement, elimination, and ether cleavage reactions were not observed. Moreover, the carbon-based solid acid was simply recovered by decantation and recycled for future reaction. The stability and reusability of the proposed catalyst was studied with four replications of conversion of 2-nitrobenzyl alcohol TMS ether to corresponding ether in the same conditions. After completion of the reaction, the catalyst was separated by filtration and used as such for subsequent experiments after adding fresh substrate and n-hexane solvent under similar reaction conditions. The yields of reaction were 85, 83, 85, and 84% for four catalytic cycles, which shows stability of the catalyst.

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