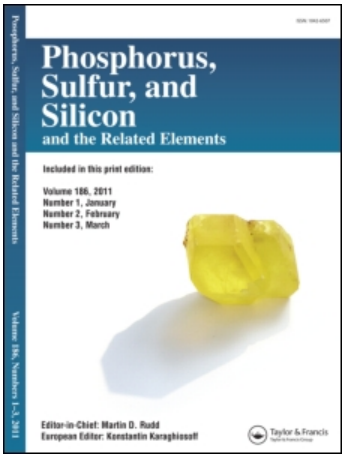

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SILICA SULFURIC ACID AS AN EFFICIENT REAGENT FOR THE SYNTHESIS OF SYMMETRICAL ETHERS UNDER MILD AND HETEROGENEOUS CONDITIONS

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(Received April 15, 2003; accepted May 15, 2003)

A mild and efficient method for the synthesis of symmetrical ethers using silica sulfuric acid is reported. All reactions are performed under compeletly heterogeneous conditions in good to high yields.

Keywords: Alcohols; heterogeneous conditions; silica sulfuric acid; symmetrical ethers

The ether linkage[1] is found prevalently in a variety of synthetic targets including oligonucleotides[2] and carbohydrates,[3] and it also is recognized as a crucial element in hydroxyl group protection.[4]

Althogh a variety of methods are capable for the synthesis of ethers,[5–7] most of them suffer from disadvantages such as long reaction times and formation of by-products. Therefore, we decided to choose a new reagent or reagent systems to overcome the above limitations. In addition for our purpose both clean and easy work-up also were important.

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 environment protection.[8] In addition, there is current research and general interest in heterogeneous systems because of the importance such systems have in industry and developing technologies.[9] In continuation of our studies on the

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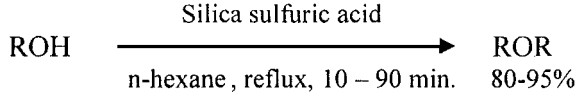
application of silica sulfuric acid,[10–14] we found that this inorganic acidic resin, as a new sulfuric acid function immobilized on the surface of silica gel via covalent bonding, can be used as a proton source for running reactions under heterogeneous conditions. Therefore, we were interested in using this reagent for the synthesis of ethers. We report here a simple and cheap method for the effective synthesis of symmetrical ethers under heterogeneous conditions.

Different types of alcohols were subjected to etherification reaction in the presence of silica sulfuric acid in refluxing *n*-hexane (Scheme 1, Table I). The etherification reactions were performed under mild and compeletly heterogeneous conditions and took place with good to excellent yields. It is noted that the formation of alkene by-products which is the common reaction in the dehydration of alcohols with H_2SO_4 was not observed during the course of the reaction.



SCHEME 1

In conclusion the lowcost and the availability of the reagents, easy and clean work-up, and high yield make this an attractive methodology. We believe that the present methodology could be an important addition to existing methodologies. The application of silica sulfuric acid in the synthesis of unsymmetrical ethers is under way.

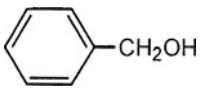
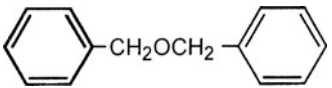
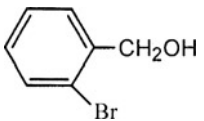
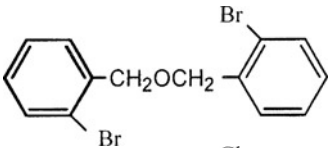
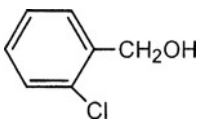
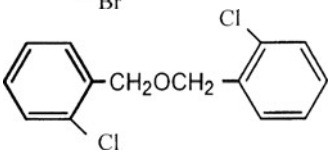
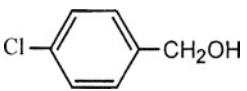
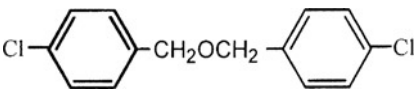
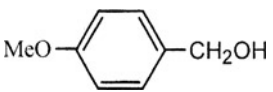
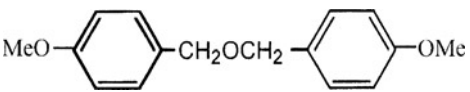
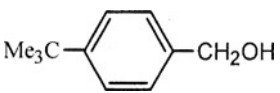
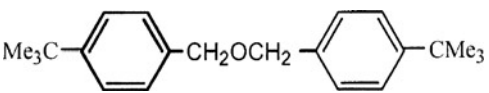
EXPERIMENTAL

Chemicals were purchased from Fluka, Merck, and Aldrich Chemical Companies. Ethers were characterized by comparison of their spectral (IR, ^{1}NMR) and physical data with that of authentic samples.

General Procedure for the Synthesis of Symmetrical Ethers

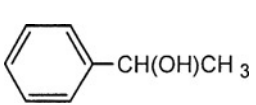
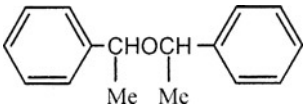
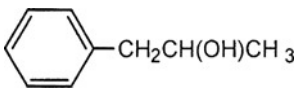
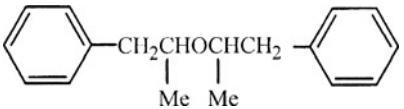
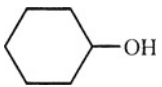
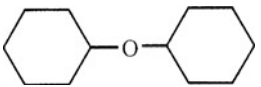
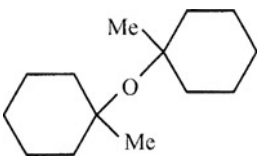
Alcohol (1 mmol) was added to a suspension of silica sulfuric acid (0.2 g) in n-hexane (3 mL). The resultant mixture was refluxed for the specified time. The progress of the reaction was monitored by TLC or GC. The reaction mixture was filtered on a silica gel pad and the residue was washed with n-hexane (10 mL). The solvent was evaporated and the ethers were obtained by distillation (Table I). If further purification

TABLE I Preparation of Symmetrical Ethers from Alcohols

Entry	Substrate	Product	Time (min)	Yield (%)[a]
1			10	90
2			10	89
3			25	95
4			40	85
5			40	90
6			10	88

(Continued on next page)

TABLE I Preparation of Symmetrical Ethers from Alcohols *(Continued)*

Entry	Substrate	Product	Time (min)	Yield (%)[a]
7			20	90
8			45	85
9	$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$	60	80
10			20	85
11			90	87
12	$PhCH{=}CHCH_2OH$	$PhCH{=}CHCH_2OCH_2CH{=}CHPh$	10	85

[a]Isolated yields.

was needed flash chromatography on silica gel provided highly pure ethers.

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