



Silica Chloride and Boron Sulfonic Acid as Solid Acid Catalysts in Preparation of Ethers and Esters Under Solvent-Free Condition

SEDIGHINIA ELHAM* and ZAHED SARGOLI MOZHGAN

Science and Research Branch, Islamic Azad University, Khouzestan, Iran

*Corresponding author: E-mail: esedighinia@yahoo.com

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Boron sulfonic acid was easily prepared from the reaction of boric acid and chlorosulfonic acid under solvent free condition. The prepared solid acid was supported on silica gel by simple grinding and used as efficient solid acid catalyst in the preparation of ethers from the aliphatic and aromatic alcohols. The ethers were prepared in high isolated yields and in lesser times. Silica chloride was prepared by refluxing of silica gel in thionyl chloride. The obtained solid acid was efficiently used for the conditions of alcohols to the corresponding ethers and acetyl esters in less reaction time and in high isolated yields.

Key Words: Boron sulfonic acid, Silica chloride, Solid acid, Alcohol, Solvent-free, Ethers, Acetyl esters.

INTRODUCTION

Etherification and acetylation are important reactions for which a wide variety of procedures have been developed during the last decades. Etherification by direct condensation of alcohols has been considered as an alternative which is conducted in the presence of catalytic amounts of organic or inorganic protic acids¹. Lewis acids have also been used for direct etherification condensation reactions^{2,3}. In most cases, the reactions suffer from the use of stoichiometric amounts of the Lewis acids which is due to their decomposition by water generated in the process of etherification reactions⁴. The most commonly used protocol is Williamson ether synthesis⁵ which requires initial transformation of alcohols into their corresponding halides or tosylates followed by their displacement with strongly basic alkoxides or phenoxides. Strong basic condition is hazardous to complex molecules carrying base sensitive functional groups.

Direct esterification of alcohols with carboxylic acids is generally avoided since the equilibrium established between the reactants and the products requires the use of excess initial compounds or removal of water from the reaction mixture to drive the process to completion⁶. Many useful methods for esterification have been reported. Some recently developed procedures utilize organic, inorganic and organometallic reagents. However, most of these methods are not free from one or more of the following disadvantages: long reaction time, severe conditions, occurrence of side processes, inaccessibility of required reagents and poor yields of the target products⁷.

Heterogeneous organic reactions have proven useful to chemists in the laboratory as well as in the industrial context. These reactions are effected by the reagents immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of the good dispersion of active reagent sites, associated selectivity and easier work-up⁸. Silica chloride and boron sulfonic acid are solid acid which can be used for different organic functional group transformations either as reagent or as catalyst under heterogeneous conditions.

EXPERIMENTAL

Silica chloride ($\text{SiO}_2\text{-Cl}$) was prepared according of the reported procedure. IR spectra were recorded on a Perkin-Elmer 8225 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were run on a Bruker Avance DPX 250 MHz instrument.

Preparation of silica chloride: To an oven-dried (120 °C, vacuum) silica gel (10 g) in a round bottomed flask (250 mL) equipped with a condenser and a drying tube, was added thionyl chloride (40 mL) and refluxed for 2 h. The unreacted thionyl chloride was distilled off. The resulting white-greyish powder was flame dried and stored in a tightly capped bottle. This silica chloride can be stored for months without decreasing its activity (**Scheme-I**).



Scheme-I

Preparation of boron sulfonic acid: A 500 mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. Boric acid (3.68 g, 60 mmol) was charged in the flask and chlorosulfonic acid (11.4 mL *ca.* 180 mmol) was added dropwise over a period of 1 h at room temperature. HCl evolved immediately. After completion of the addition, the mixture was shaken for 1 h, while the residual HCl was eliminated by suction. Then the mixture was washed with diethyl ether to remove the unreacted chlorosulfonic acid. Finally, a greyish solid material was obtained in 91% yield (0.8 g).

General procedure

Etherification: A mixture of 1 mmol of alcohol, 0.5 g of silica gel and 0.8 g B(HSO₄)₃ or 0.5 g of silica chloride were pulverized in a mortar for 5 min. It was heated to 60 °C in an

oil bath for a specific time. The progress of reactions was monitored by TLC. After completion of the reaction, chloroform (10 mL) was added and then, the mixture was filtered and the solid precipitate was washed with 2 × 10 mL of chloroform. After evaporation of solvent under reduced pressure, the desired ethers were obtained in high isolated yields (Table-1).

Acetylation: A mixture of silica chloride (1 g) and glacial acetic acid are placed in 50 mL round bottomed flask was stirred for 5 min. Then alcohol (1 mmol) is added to solution and reaction solution was stirred under reflux condition for specified time. The progress of reaction was monitored by TLC and then filtered. The filtrate was washed with CHCl₃ (2 × 5 mL) then water (10 mL) was added. The organic layer dried over anhydrous CaCl₂ and evaporation of the solvent on a rotary evaporator afforded a residue. The yields were 70-89 % (Table-2).

TABLE-1
ETHERIFICATION OF ALCOHOLS IN PRESENCE OF SILICA CHLORIDE AND
BORON SULFONIC ACID UNDER SOLVENT-FREE CONDITIONS

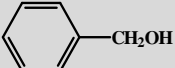
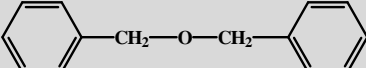
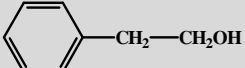
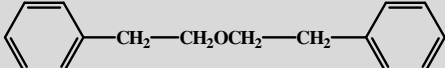
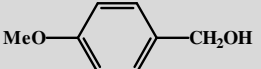
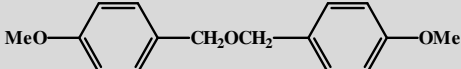
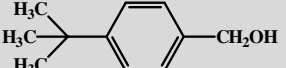
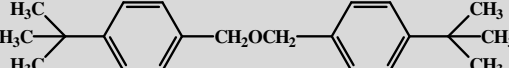
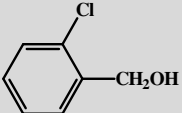
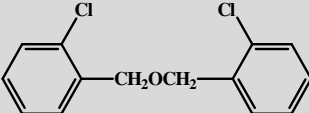
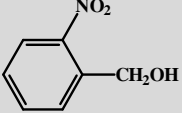
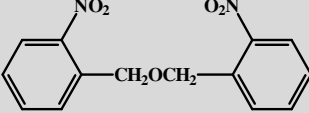
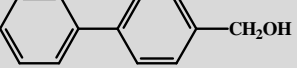
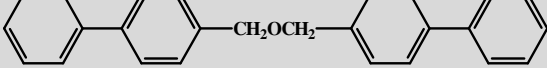


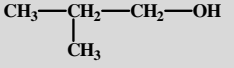
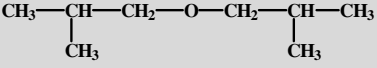
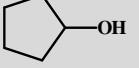
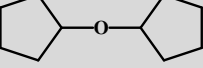
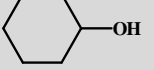
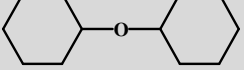
| Initial substances | Product | Silica chloride | | Boron sulfonic acid | |
|---|--|-----------------|-----------|---------------------|-----------|
| | | Time (min) | Yield (%) | Time (min) | Yield (%) |
|  |  | 7 | 87 | 9 | 87 |
|  |  | 6 | 85 | 7 | 95 |
|  |  | 10 | 84 | 13 | 88 |
|  |  | 9 | 85 | 10 | 96 |
|  |  | 9 | 82 | 11 | 95 |
|  |  | 17 | 87 | 19 | 91 |
|  |  | 7 | 89 | 9 | 92 |
|  |  | 5 | 84 | 7 | 87 |
|  |  | 8 | 73 | 10 | 82 |
|  |  | 13 | 79 | 1 | 87 |
|  |  | 15 | 64 | 17 | 80 |

TABLE-2
 ACETYLATION OF ALCOHOLS WITH ACETIC ACID IN PRESENCE OF SILICA CHLORIDE

| Initial substances | Product | Time (min) | Yield (%) |
|-----------------------------------|---------|------------|-----------|
| $\text{CH}_3\text{CH}_2\text{OH}$ | | 50 | 89 |
| | | 50 | 77 |
| | | 55 | 70 |
| | | 55 | 70 |
| | | 60 | 71 |
| | | 50 | 79 |
| | | 55 | 78 |
| | | 55 | 80 |
| | | 50 | 81 |
| | | 50 | 82 |
| | | 60 | 73 |
| | | 70 | 80 |

RESULTS AND DISCUSSION

In this work, an inorganic silica based solid acids and boron sulfonic acid have been introduced, which are of great importance in terms of convenience, cheapness, non-toxicity, easy production, handling and insolubility in all organic solvents. Silica chloride and $\text{B}(\text{HSO}_4)_3$ have been used as a catalysts for the preparation of ethers and acetyl esters with special properties.

Due to the less cost and availability of the reagent, heterogeneous nature, mild reaction conditions, short reaction times, excellent *in situ* proton generation and ability for substitution of nucleophiles, these catalysts can be used for different purposes in organic chemistry.

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