

Protection Carbonyl Group by $\text{Mg}(\text{HSO}_4)_2$ as Solid Acid Versus with Mg HPO_4

Fariba Jafari, Zhila safari, and Najaf Hedayat

Abstract—Two solid acid $\text{Mg}(\text{HSO}_4)_2$ and MgHPO_4 are prepared from the reaction of H_2SO_4 and H_3PO_4 with MgCl_2 , respectively. These acids are supported on the Silica gel layer and used as catalyst for protection of carbonyl compounds. These supported catalyst on Silica gel layer are used for transformation of aldehydes and ketones to ring acetal and ketal forms in conditions of solvent free. The cooperation of MgHPO_4 catalyst with $\text{Mg}(\text{HSO}_4)_2$ shows that the time of the reaction become lower and product yield become higher.

Keywords— $\text{Mg}(\text{HSO}_4)_2$, MgHPO_4 , Solvent free, acetalization, solid acid, protection

I. INTRODUCTION

RECENTLY, Some chemists found that many reaction proceed efficiently in the solid state. Indeed, in many cases, solid state organic reaction occurs more efficiently and more selectively than does its solution counterpart. The solvent-free reaction has many advantages such as reduced pollution, low cost, process simplicity and easier work-up. These factors are especially important in industry. Acetals are not only the most widely used protecting groups but are also efficient Chiral auxiliary groups for enantioselective synthesis[1]. The most convenient and practical method for acetalization is the reaction of carbonyl compounds with alcohols in the presence of an appropriate catalyst[2]. There are some reported in the literature of application of some catalysts for this purpose such as, tetrabutylammonium tri bromide[3], polymer bounded metal complexes[4], SbCl_3 [5], silica gel supported metallic sulfates[6], DDQ [7], NBS [8], lithium tri fluoride [9], iodine[10], titanium cation-Exchange montmorillonite[11] and polyaniline supported sulfuric acid salt[12] are usually utilized as catalysts. Solid acid have many advantages such as simplicity in handling, Decreasing reactor and plant corrosion problems, and environmentally safe disposal[13]. Also, wastes and by-products can be minimized or avoided by developing cleaner. Synthesis routes. 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.

Fariba Jafari, Department of Chemistry, Dezful Branch, Islamic Azad University, Dezful, Iran. e-mail: faribajafari@yahoo.com

Habib Khamisi, Dezful Branch, Islamic Azad University, Dezful, Iran.

Najaf Hedayat, Department of Agriculture, Dezful Branch, Islamic Azad University, Dezful, Iran. N.hedayat@yahoo.com. Tel:+989166443227

Very recently, we among many others have demonstrated that heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and minimization of chemical wastes as compared to liquid phase counterparts[13].

II. EXPERIMENTAL

$\text{Mg}(\text{HSO}_4)_2$ [14] and MgHPO_4 were synthesized according to the previously reported procedure. The acetalization products were characterized by comparison of their spectral (IR, ¹H NMR), TLC and physical data with the authentic samples.

A. Preparation of Magnesium hydrogen sulfate

A 50ml 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. Anhydrous magnesium chloride (4.0 g, 40 mmol) was charged in the flask and concentrated sulfuric acid (98%, 7.35 g, 40 mmol) was added dropwise over a period of 30 min at room temperature. HCl evolved immediately. After completion of the addition, the mixture was shaken for 30 min, while the residual HCl was eliminated by suction. The $\text{Mg}(\text{HSO}_4)_2$ (6.46g) was obtained as white gel. The obtained solid acid was mixed by silicagel (6.43g).

B. Preparation of Magnesium hydrogen phosphat

A 50ml 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. Anhydrous magnesium chloride (4.0 g, 40 mmol) was charged in the flask and concentrated phosphoric acid (85%, 7.35 g, 40 mmol) was added dropwise over a period of 30 min at room temperature. HCl evolved immediately. After completion of the addition, the mixture was shaken for 30 min, while the residual HCl was eliminated by suction. The MgHPO_4 (5.48g) was obtained as white gel. The obtained solid acid was mixed by silicagel (6.43g).

C. Typical procedure for the protection of aldehyde and ketones at room temperature and under solvent-free condition

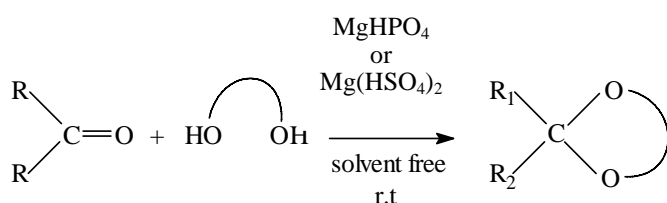
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III. RESULTS AND DISCUSSION

Although there are a few reports on the application of inorganic acidic salts such as $\text{Mg}(\text{HSO}_4)_2$ or MgHPO_4 in synthetic methodology recently more attention has been paid to the investigation of their potentials in organic synthesis. These salts are stable and non-hygroscopic solid material, insoluble in most organic solvent. By have the above facts in mind, now we wish to report a convenient method for synthesis of acetals and ketals using $\text{Mg}(\text{HSO}_4)_2$ and MgHPO_4 , at room temperature and under solvent-free conditions (Scheme 1).



R, R₁, R₂ = alkyl, aryl, H

Scheme 1

Different Kinds of alcohols a carbonyl compounds were subjected to acetalization reaction in the presence of $\text{Mg}(\text{HSO}_4)_2$ and MgHPO_4 at under solvent-free conditions.

As shown in tabel 1, different class of aldehydes and ketones can be efficiently protected as acetal and ketal by alcohols in the presence of $\text{Mg}(\text{HSO}_4)_2$ and MgHPO_4 under solvent-free condition and pure products were obtained by product extraction by CCl_4 , simple filtration and solvent evaporation. And Used as of $\text{Mg}(\text{HSO}_4)_2$ product yield goes higher and the time reaction will decrease in compare to MgHPO_4 . In conclusion, an inexpensive and easy procedure for the effective conversion of carbonyl derivatives to their corresponding acetals and ketals has been achieved. The cheapness and availability of the catalyst with easy procedure and work-up make this method attractive in organic synthesis. We believe that the present solvent-free methodology would be an important addition to existing methodologies.

TABLE I
ACETALIZATION OF ALCOHOLS IN THE PRESENCE $\text{Mg}(\text{HSO}_4)_2$
AND MgHPO_4

Entry	Alcohol 2 mmol	Product 1 mmol	Time/Yield% (min) $\text{Mg}(\text{HSO}_4)_2$	Time/Yield% (min) MgHPO_4
1			5-82	5-80
2			5-94	5-90
3			5-85	5-81
4			5-82	5-80
5			10-82	10-79
6			5-83	5-80
7			5-87	5-84
8			5-85	5-82
9			5-88	5-85

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