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Short Report

$Al(HSO_4)_3$ as an Efficient Catalyst for Acetalization of Carbonyl Compounds under Heterogeneous or Solvent -Free Conditions

BiBi Fatemeh Mirjalili[,a], **Mohammad Ali Zolfigol**[b], **Abdolhamid Bamoniri**[c] and **Azizeh Hazar**[a]*

[a]*Department of Chemistry, College of Science, Yazd University, POBox 89195-741 Yazd, Iran*

[b]*Department of Chemistry, College of Science, Bu-Ali Sina University, POBox 4135, 65174 Hamadan, Iran*

[c]*Department of Chemistry, College of Science, Kashan University, 51167 Kashan, Iran*

O ácido $Al(HSO_4)_3$ sólido foi usado na acetalização de compostos carbonílicos à temperatura ambiente, sem solvente, levando aos produtos desejados em excelentes rendimentos. A disponibilidade e baixo custo deste reagente, aliados a processo simples e fácil torna o método atraente para a síntese orgânica.

$Al(HSO_4)_3$ as a solid acid was applied for acetalization of carbonyl compounds at room temperature and under solvent-free conditions with good to excellent yields. The cheapness and availability of this reagent with easy procedure and work-up make this method attractive for the organic synthesis.

Keywords: acetalization, solvent-free, solid acid, $Al(HSO_4)_3$, carbonyl compound, heterogeneous condition

Introduction

Recently, some chemists found that many reactions 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 ethylene glycol in the presence of an appropriate catalyst, with removal of water formed. Tetrabutylammonium tribromide,[2] polymer bounded metal complexes,[3] $SbCl_3$,[4] silica gel supported metallic sulfates,[5] DDQ,[6] NBS,[7] lithium triflate,[8] iodine,[9] titanium cation-exchange montmorillonite[10] and polyaniline supported sulfuric acid salt[11] are usually utilized as catalysts.

Solid acids have many advantages such as simplicity in handling, decreasing reactor and plant corrosion problems, and environmentally safe disposal.[12] 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.

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 the liquid phase counterparts.[13] Thus, inorganic acidic salts such as $Al(HSO_4)_3$[14] or $Mg(HSO_4)_2$[15] could be recommended for the above mentioned purposes.

Results and Discussion

Although there are a few reports on the application of inorganic acidic salts such as $Mg(HSO_4)_2$ or $Al(HSO_4)_3$ in synthetic methodology, recently more attention has been paid to the investigation of their potentials in organic synthesis.[14-17] These salts are stable and non-hygroscopic solid material, insoluble in most organic solvents. In continuation of our studies on the application of metallic hydrogensulfate salts in organic synthesis, now we wish

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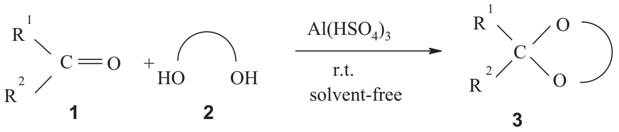
* e-mail: fmirjalili@yazduni.ac.ir

to report a convenient method for synthesis of acetals and ketals using $Al(HSO_4)_3$, at room temperature and solvent-free conditions (Scheme 1).



Scheme 1.

Different kinds of diols and carbonyl compounds were subjected to the acetalization reaction in the presence of $Al(HSO_4)_3$ at room temperature and under solvent-free conditions. Meanwhile, the same acetals and ketals were synthesized in the presence of $Al(HSO_4)_3$ in *n*-hexane as a solvent under thermal condition (Table 1). The highly pure acetals and ketals can be obtained by washing the mixture with hot n-hexane, diethylether or dichloromethane, followed by simple filtration and evaporation of the solvent. In order to show the chemoselectivity of the method we have carried out the successful acetalization of *p*-nitrobenzaldehyde in the presence of *p*-nitroacetophenone (Table 1, entry p). As it is shown in table, in solvent-free condition, the chemoselectivity is higher than the thermal condition.

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 reagents with easy procedure and work-up make this method attractive for the large-scale operation. We believe that the present solvent-free methodology would be an important addition to existing methodologies.

Experimental

General

Chemicals such as carbonyl compounds, ethylene glycol, 1,3-butanediol and guaiacol glyceryl ether, phenyl ethylene glycol, aluminium chloride and sulfuric acid were purchased from Fluka, Merck and Aldrich chemical companies. 5-norbornene-2,2-dimethanol[18] and $Al(HSO_4)_3$[14] was 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.

Preparation of aluminum hydrogensulfate

A 50 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. Anhydrous aluminum chloride (3.34 g, 0.025 mol) was charged in the flask and concentrated sulfuric acid (98%, 7.35 g, 0.075 mol) 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. Finally, a pale-brown solid material was obtained in 7.7 g. $Al(HSO_4)_3$ was characterized according to the previously reported procedure.[14]

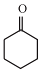
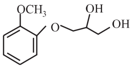
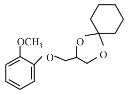
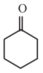
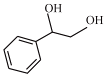
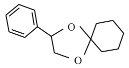
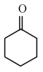
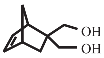
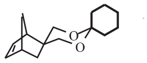
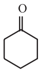
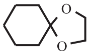
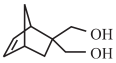
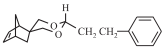
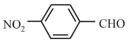
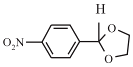
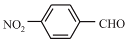
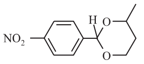
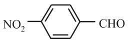
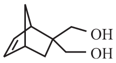
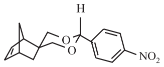
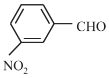
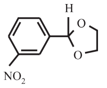
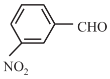
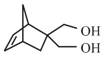
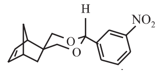
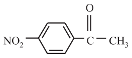
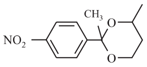
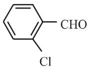
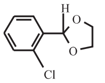
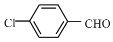
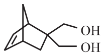
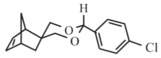
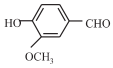
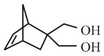
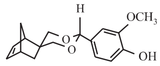
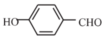
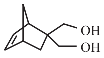
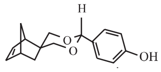
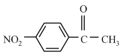
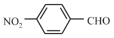
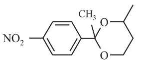
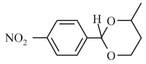
*Typical procedure for the preparation of acetal (**3g**) from 4- nitrobenzaldehyde at room temperature and solvent – free condition*

In a mortar, a mixture of 4- nitrobenzaldehyde (0.151 g, 1 mmol), 1,3-butanediol (0.18 mL, 2 mmol), and $Al(HSO_4)_3$ (0.3 g) was pulverized for 5 minutes. The reaction progress was followed by TLC. After completion of the reaction, diethyl ether was added and the heterogeneous mixture was filtered. By removal of solvent, addition of ethanol and water, the acetal was obtained as pure crystal. Yield: 0.2 g (90%); mp: 107-109 ºC. IR ν_{max} / cm^{-1}: 3050 (w) (=CH stretching), 3000-2900 (m) (-CH stretching), 1600 (m) (C=C stretching), 1530 (s) (asymmetric stretching NO_2 group), 1350 (s) (symmetric stretching NO_2 group), 1100 (s) (C-O, stretching). ^1H NMR (90 MHz, $CDCl_3$), δ1.2 (d, 3H, *J* 6.7Hz), 1.56 – 1.74 (m, 2H), 3.9-4.1(m, 3H), 5.5 (s, 1H), 7.6 (d, 2H, *J* 6.8 Hz), 8.1(d, 2H *J* 6.8 Hz).

*Typical procedure for preparation of ketal (**3k**) from 4- nitroacetophenone under thermal condition*

A suspension of 4-nitroacetophenone (0.16 g, 1 mmol), 1,3-butanediol (0.18 mL, 2 mmol) and $Al(HSO_4)_3$ (0.2 g) in n-hexane (10 mL) was stirred under reflux condition. The progress of reaction was followed by TLC. After 30 minutes of reflux, the heterogeneous mixture was filtered and washed with hot n-hexane. By removal of solvent, the crude product was isolated. The pure ketal was obtained by column chromatography (eluent, ether:petroleum ether, 30:70); yield: 0.2 g (85%); mp 97-99 ºC; IR ν_{max} / cm^{-1}: 3100 (w) (=CH stretching), 3000-2800 (m) (-CH stretching), 1600 (m) (C=C stretching), 1530 (s) (asymmetric stretching NO_2 group), 1500 (w) (C=C stretching), 1350 (s) (symmetric stretching NO_2 group), 1200 and 1100 (s) (C-O, stretching). ^1H NMR (90 MHz, $CDCl_3$), δ 1.14 (d, 3H, *J* 6.7 Hz), 1.44 (s, 3H), 1.62 – 1.7 (m, 2H), 3.5-4 (m, 3H), 7.57 (d, 2H, *J* 6.8 Hz), 8.1(d, 2H, *J* 6.8 Hz).

Table 1. Conversion of carbonyl compounds to acetals and ketals by using $Al(HSO_4)_3$

Entry	Carbonyl compound(**1**)	Diol(**2**)	Product(**3**)	r.t. and solvent free condition *Carbonyl compound* (mmole)/ Diol (mmol)/$Al(HSO_4)_3$ (g) [Time (min)/Yield(%)[a]]	Thermal condition *Carbonyl compound* (mmole)/ Diol (mmol)/$Al(HSO_4)_3$ (g) [time (min)/Yield (%)[a]]	*Ref.*
a				1/1.2/0.2 [10/88]	1/1.2/0.2 [45/85]	20
b				1/1.2/0.2 [10/75]	1/1.2/0.2 [60/62]	21
c				1/1.2/0.2 [10/65]	1/1.2/0.2 [40/60]	20
d		HO CH_2 CH_2 OH		1/2/0.34 [10/70]	1/2/0.2 [60/64]	20
e	$PhCH_2CH_2CHO$			1/1.2/ 0.2 [8/85]	1/1.2/0.2 [30/81]	20
f		HO CH_2 CH_2 OH		1/2/0.2 [5/90]	1/2/0.2 [60/90]	20
g		CH_3 CHOH CH_2 CH_2OH		1/2/0.3 [5/90]	1/1.2/0.2 [30/91]	-
h				1/1.2/0.2 [5/86]	1/1.2/0.2 [30/85]	19
i		HO CH_2 CH_2 OH		1/2/0.2 [6/81]	1/2/0.2 [60/85]	20
j				1/1.2/0.2 [7/89]	1/1.2/0.2 [45/85]	19
k		CH_3 CHOH CH_2 CH_2OH		1/2/0.2 [10/50]	1/2/0.2 [30/85]	-
l		HO CH_2 CH_2 OH		1/2/0.2 [7/72]	1/2/0.2 [60/81]	20
m				1/1.2/0.2 [9/78]	1/1.2/0.2 [45/84]	19
n				1/1.2/0.2 [10/55]	1/1.2/0.2 [30/82]	19
o				1/1.2/ 0.2 [10/58]	1/1.2/0.2 [30/80]	19
p	 	CH_3 CHOH CH_2 CH_2OH	 	1/1/1.2/0.2 [10/7] [10/85]	1/1/1.2/0.2 [30/35] [30/58]	

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[a]isolated yield.

Acknowledgments

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