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Comparative Catalytic Performance of Silica-HNO_3 and Silica-HCl for the Synthesis of Acylals from Aromatic Aldehydes

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Abstract

Acylal is one of the most effective protecting groups for carbonyl functionality in organic synthesis. In this work an attempt was made for the first time to compare the performance of silica-HNO_3 and silica-HCl as heterogeneous catalysts in the formation of acylals from aromatic aldehydes. Thus the silica-acid mixtures were prepared by mixing the column chromatographic grade silica gel with concentrated HNO_3 and concentrated HCl to obtain free flowing powders. These powders at different ratios were used to investigate the formation of acylal from 3-nitrobenzaldehyde as a model reaction under different operating parameters. Subsequently, the optimum condition was applied in the conversion of some substituted aromatic aldehydes to their corresponding acylals. It was found that the two catalytic systems displayed almost similar catalytic performance affording the highest yield of the acylal at 83%.

Keywords: Acylal, Silica, Brönsted acid, Aromatic aldehyde

1. Introduction

Acylals are commonly employed as one of the protecting groups for carbonyl compounds due to their stability under various reaction conditions [1]. In addition to their role as protecting group, they are also important precursors for the synthesis of chiral alicyclic esters, dienes, and as cross linking reagents for the cellulose in cotton [2-5]. Thus the development of new synthetic methodologies for acylal synthesis continued to receive appreciable attention, among which solid supported catalysis has been of particular interest. The advantages of this methodology include safety, atom economy, easy work-up procedures, and short reaction duration. Hence this led to the development of some heterogenous catalysts such as SnCl4/SiO2 [6], zinc montmorillonite [7], sulfonic acid functionalized ionic liquids [8], zirconium sulfate tetrahydrate-silica gel [9], silica-*S*-sulfonic acid [10], silica-perchloric acid [11], copper *p*-toluenesulfonate/HOAc [12], H3PW12O40 - MCM-41 [13], solid superacids [14], $NaHSO_4$-SiO_2 [15], silica-supported boron sulfonic acid [16], MCM-41-SO_3H [17], Nano-Fe_3O_4-encapsulated silica [18], Tungstosulfonic acid [19], PEG-SO_3H [20], Phospho sulfonic acid [21], $Mg(CH_3SO_3)_2$–HOAC [22], propylsulfonic acid based nanosilica [23], ZSM-5-SO_3H [24], sulfonic acid based nanoporous carbon [25] have been reported for the synthesis of acylals.

Literature search revealed that silica supported Brönsted acids are less investigated despite their cheapness compared to the other acid catalysts. Therefore in this work, we attempted to document the efficiency of silica-HNO_3 and silica-HCl systems for the synthesis of acylals from aromatic aldehydes.

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2. Material and Method

2.1. General

All chemicals were purchased from Sigma-Aldrich (Darmstadt, Germany) and used without further purification. NMR spectra (^1H) were recorded on a 400 spectrometer (Bruker AVANCE). Perkin–Elmer BX spectrophotometer was used for the recording of the FTIR spectra.

2.2. Preparation of Silica-Brönsted acid Catalysts

Silica (column chromatographic grade, 230–400 mesh) and appropriate Brönsted acid were mixed in grams at the respective ratio. The respective mixtures were stirred for 15 min and then heated on a hot plate gently. While heating, the mixtures were swirled to afford free-flowing white solids. The solids were further dried in an oven (120 °C) for 48 h [15].

2.3. General Procedure for the Synthesis of Acylals

The aromatic aldehyde (10 mmol), acetic anhydride (40 mmol) and silica-Brönsted acid (25%/wt) were mixed and stirred at room temperature. And the progress of the reaction was monitored by TLC Hexane: EtOAc (9:1) After the completion of the reaction, the mixture was treated with ethylacetate, and the catalyst was filtered. Subsequently, the filtrate was washed with saturated $NaHCO_3$ solution and water and finally dried over anhydrous Na_2SO_4. The solvent was then evaporated using a rotary evaporator to obtain the crude product which was purified by column chromatography to give the pure acylal [15]. The spectral data of the synthesised compounds were compared with the literature [6,7,9,10-26].

3. Results and Discussion

3.1. Effect of Silica-Brönsted acid Ratio

Considering that the acid catalyst is required for the activation of the carbonyl functionality to enable the formation of the diacetate bonds, it was thus decided to investigate the appropriate ratio of the silica-Bronsted acid to be effective. As observed in Table 1, the reaction of 3-nitrobenzaldehyde was taken as the model reaction. The two Bronsted acids were found to give equal yields of the corresponding acylals at 2:1 ratio. Although not indicated in the Table, but it was found that any attempt to raise the ratio above 2:1, the yield of the acylal deteriorates. Hence it was decided to lower the weight of the silica while increasing the weight of the Bronsted acids. After three attempts, it was found that yields remains unchanged. Therefore the most effective ratio was 2:1 with both silica-HNO_3 and silica-HCl giving equal yields (43%) of the acylal.

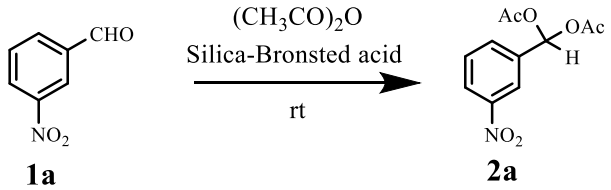


Figure 1. Synthesis of acylal from 3-Nitrobenzaldehyde

Table 1. Effect of Silica-Brönsted acid Ratio[a]

W/W (g)[b]	Silica-HNO_3	Silica-HCl
	Yield (%)[c]	Yield (%)[c]
2:1	43	43
1.9:1.1	28	36
1.8:1.2	28	36
1.7:1.3	28	36

[a] 3-Nitrobenzaldehyde (10 mmol), acetic anhydride (40 mmol), silica- Brönsted acid (25%/w), 10 min
[b] Silica-Brönsted acid
[c] Isolated compound

3.2. Effect of Duration

The model reaction was further tested at lower time intervals. While silica-HNO_3 gave the same yield as at 10 minutes (43%), the silica-HCl furnished the product with depreciable yield (35%). After three attempts to lower the time intervals, both the catalysts system gave unchanged yields (Table 2).

Table 2. Effect of Duration[a,b]

Minutes	Silica-HNO_3	Silica-HCl
	Yield (%)[c]	Yield (%)[c]
9	43	35
8	27	35
7	27	35
6	27	35

[a] 3-Nitrobenzaldehyde (10 mmol), acetic anhydride (40 mmol), silica- Brönsted acid (25%/w)
[b] Silica-Brönsted acid ratio (2:1)
[c] Isolated compound

3.3. Effect of Solvent

The effect of solvent on the formation of the acylal of the model reaction was also investigated. Thus three solvents of different polarities were used (Table 3). In the case of silica-HNO_3, it appears that acetonitrile afforded the product with the highest yield (46%), while silica-HCl gave the corresponding acylal with a yield similar to the solvent-free system. The yield for the silica-HNO_3 catalyst was however not considered so significantly different from that of the solvent-free reactions (43%). Generally in the case of silica-HCl, all of the solvent system afforded the acylal with lower yield compared to the solvent-free system. This phenomenon was also observed in a related study [26].

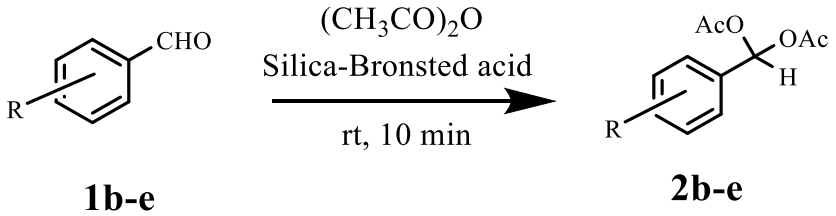
Table 3. Effect of Solvent[a]

Solvent	Silica-HNO_3	Silica-HCl
	Yield (%)[c]	Yield (%)[c]
Ethylacetate	13	28
Methanol	21	28
Acetonitrile	46	35

[a] 3-Nitrobenzaldehyde (10 mmol), acetic anhydride (40 mmol), silica- Brönsted acid (25%/w), 10 min
[b] Silica-Brönsted acid ratio (2:1)
[c] Isolated compound

3.4. Substrate Scope

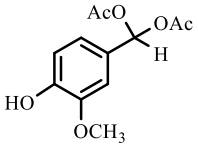
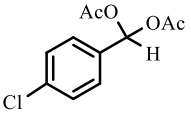
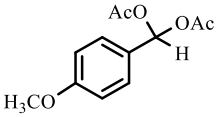
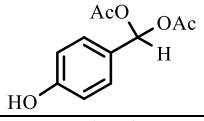
The optimum condition established was adopted in order to assess the implication of the reaction on other aromatic aldehydes containing different substituents (Table 4). It was thus found that methoxy substituted aldehyde furnished the highest yield of the acylal (83%) for both the catalytic systems followed by the hydroxy derivative. The rest of the derivatives were poorly converted to the corresponding acylals.



1b-e **2b-e**

Figure 2. Synthesis of acylals from Substituted Aromatic Aldehydes

Table 4. Substrate Scope[a,b]

Entry	Acylal	Silica-HNO_3 Yield (%)[c]	Silica-HCl Yield (%)[c]
2b		20	13
2c		Traces	12
2d		83	83
2e		78	77

[a] Aromatic aldehyde(10 mmol), acetic anhydride (40 mmol), silica- Brönsted acid (25%/w), rt, 10 min
[b] Silica-Brönsted acid ratio (2:1)
[c] Isolated compound

4. Conclusion

This work attempted to document the performance of two catalytic systems in the formation of acylals which until now have never been reported. The silica-HNO3 and silica-HCl mixtures were prepared following a reported procedure. Consequently, the silica supported acid powders were used as catalyst in the conversion of the carbonyl functionality of the aromatic aldehydes into acylal. The optimum condition of the reaction was investigated by studying three operating parameters namely, silica-Brönsted acid ratio, duration, and solvent effects. Subsequently, some structurally different aromatic aldehydes were subjected to the reaction condition to afford the corresponding acylals. Generally, the two catalytic systems were able to effect the formation of the acylals of some of the aldehydes appreciably, while other aldehydes appeared to furnish poor yields of the products.

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