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Magnetic nanoparticle immobilized *N*-propylsulfamic acid: The chemoselective, efficient, green and reusable nanocatalyst for the conversion of aldehydes to their 1,1-diacetates (acetylals) under solvent-free

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Abstract : Highly efficient and mild acetylation of aldehydes with acetic anhydride catalysed by *N*-Propylsulfamic acid supported on to magnetic Fe₃O₄ nanoparticles (MNPs-PSA) was performed under neutral conditions to produce corresponding 1,1-diacetates (acetylals) in good to excellent yields. The magnetic nanocatalyst can be readily recovered easily by applying an external magnet device and reused for

at least 10 reaction runs without considerable loss of reactivity.

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Keywords : Magnetic nanoparticles; Nanocatalyst; *N*-Propylsulfamic acid; Acetylation of aldehydes; One-Pot Synthesis; Solvent Free.

INTRODUCTION

The carbonyl group is one of the most versatile functional groups in organic chemistry and a great deal of synthetic work has been performed and masking of the carbonyl compounds^[1]. In these methods, formation of 1,1-diacetates from aldehydes and acetic anhydride is one of the most useful aspect.

As synthetic intermediates or protecting groups for aldehydes, 1,1-diacetates are stable in neutral and basic media, and easy to convert to parent aldehydes^[2-6]. Usually, 1,1-Diacetates are synthetically useful precursors for the synthesis of dienes for Diels-Alder cycloaddition reactions^[7].

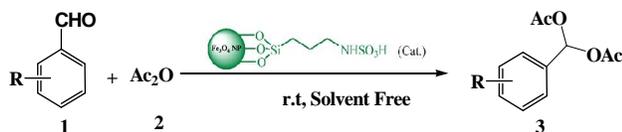
Usually gem-diacetate are synthesized from condensation of aldehydes and acetic anhydride in the presence of both protonic and Lewis acids such as sulphuric acid^[8,9], phosphoric acid and methane sulphonic acid^[10], NH₂SO₃H^[11], and Lewis acids, such

as Bi(NO₃)₃·5H₂O^[12], ZrCl₄^[13], FeCl₃^[14], anhydrous FeSO₄^[15], Bi(OTf)₃^[16], PCl₃^[17], and LiBr^[18].

Although in many case the gem-diacetate are obtained in good yield but many of these method suffer from some of the following disadvantages: Long reaction time, tedious work-up, use of homogenous catalyst, reflux condition and use of harmful solvents.

RESULTS AND DISCUSSION

In continuation of our research on various transformations,^[19-23] herein is reported the use of MNPs-PSA^[24] as a more robust and efficient catalyst in the acetylation of aldehydes 1a-k with acetic anhydride to produce corresponding 1,1-diacetates (acetylals) in good yields under solvent free (Scheme 1, TABLE 1). As shown in the Table, the reactions occurred excellently within 1-7 min under solvent free conditions. The experimental results indicate that the



Scheme 1

most effective conversion occurred when a mole ratio 1:0.75 % mol of substrate/ MNPs-PSA was used. Longer reaction times were required when lower amounts of MNPs-PSA were employed. It is important to note that no acetylals derivatives were afforded when the reactions were performed in the absence of MNPs-PSA in the reaction mixture.

Unfortunately, when acetophenone was used in this reaction, no corresponding product was isolated (Entry 11). In the case of substrates bearing aldehyde and ketone functionalities, the keto group remains unaffected and aldehyde is converted into 1,1-diacetal. This result indicates that the chemoselective protection of an aldehyde in the presence of ketone could be achieved by this procedure (Scheme 2).

MATERIAL AND METHODS

The employed chemicals were obtained from either *Merck* or *Fluka*. The IR spectra were recorded using a *Shimadzu 435-U-04* spectrophotometer (KBr pellets) and the NMR spectra were obtained in CDCl_3 using a 400 MHz *JEOL FT NMR* spectrometer. All melting points were determined on a Büchi 530 melting point apparatus and are reported uncorrected.

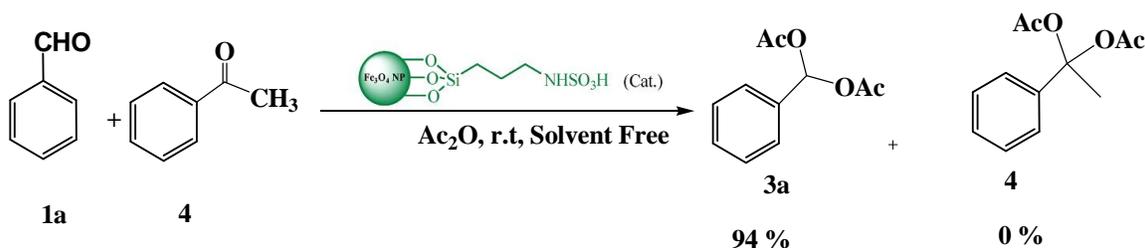
Conversion of aldehydes 1a–k to acetylals 3a–k with Ac_2O catalysed by MNPs-PSA. General procedure

To a mixture of aldehyde (5 mmol) and acetic anhydride (1.02 g, 10 mmol), MNPs-PSA (0.75 % mol, 3.9 mg) was added and the mixture was pulverized with a pestle at room temperature for the specified time. Completion of the reaction was indicated by TLC (EtOAc/petroleum ether (1:9)). After the reaction was completed, EtOH was added and the catalyst was

TABLE 1 : MNPs-PSA catalyzed for the conversion of aldehydes 1a–k to 1,1-diacetals (acetylals) 3a–k with Ac_2O under solvent-free conditions

Entry	Product ^a	Aldehyde	t / min	Yield ^a , %	M.P., °C
1	3a	$\text{C}_6\text{H}_5\text{CHO}$	5	94	226-228
2	3b	4- $\text{ClC}_6\text{H}_4\text{CHO}$	2	93	258-260
3	3c	4- $\text{FC}_6\text{H}_4\text{CHO}$	3	96	213-215
4	3d	4- $\text{ClC}_6\text{H}_4\text{CHO}$	2	95	253-256
4	3e	4- $\text{MeC}_6\text{H}_4\text{CHO}$	5	93	237-238
5	3f	2- $\text{NO}_2\text{C}_6\text{H}_4\text{CHO}$	2	92	106-108
6	3g	4- $\text{NO}_2\text{C}_6\text{H}_4\text{CHO}$	6	95	240-242
7	3h	3- $\text{NO}_2\text{C}_6\text{H}_4\text{CHO}$	1	94	235-237
8	3i	4- $\text{OMeC}_6\text{H}_4\text{CHO}$	1	92	199-201
9	3j	4- $(\text{CH}_3)_2\text{N-C}_6\text{H}_4\text{CHO}$	7	92	234-236
10	3k	4- $\text{BrC}_6\text{H}_3\text{CHO}$	5	93	253-255
11	4	$\text{C}_6\text{H}_5\text{COCH}_3$	60	0	--

^aAll the products are known and were characterized by IR, ^1H NMR and ^{13}C NMR comparisons with those of authentic samples^[20]



Scheme 2

FULL PAPER

separated by an external magnet. Aqueous EtOH 15% was added to the crude product; the precipitate was separated and then recrystallized using aqueous EtOH 15% for two times. The products were characterized on the basis of their physical and spectral analysis and by direct comparison with literature data^[2-10,20].

CONCLUSION

The present methodology shows that nano Fe₃O₄ (MNP) is an efficient catalyst in the acetylation of aldehydes with acetic anhydride to produce corresponding 1,1-diacetates under solvent-free in room temperature. The main advantages of the presented protocol are mild, clean and environmentally benign reaction conditions, as well as the high yields. Furthermore, this method is also expected to find application in organic synthesis due to the low cost of the reagent. It is believed that this method will be a useful addition to modern synthetic methodologies.

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