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# Facile Synthesis of 1,1-Diacetates from Aldehydes Using Environmentally Benign Solid Acid Catalyst Under Solvent-Free Conditions

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# ABSTRACT

Variety of aromatic and aliphatic aldehydes are converted into their 1,1-diacetates in the presence of environmentally benign  $Mo/TiO_2-ZrO_2$  solid acid catalyst in good to excellent yields under solvent-free conditions.

*Key Words:* 1,1-Diacetates; Carbonyl group; Solid acid Catalyst; Solvent-free conditions.

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### INTRODUCTION

The carbonyl group plays a predominant role in organic synthesis due to its electrophilic nature and one of the most common problems in multi-step synthetic processes is protecting the carbonyl group from nucleophilic attack until its electrophilic property could be utilized. Therefore, protection and deprotection of carbonyl group is an area of interest in synthetic organic chemistry.<sup>[1]</sup> Protecting group is also very useful in separation and purification of products particularly in multi-step liquid phase methodologies.

Various procedures including acetalization and thioacetalization are known for protection of carbonyl groups.<sup>[1–3]</sup> In recent years, gem-diacetates are gaining more attention in the protection of aldehydes. The main advantage in diacetalization of aldehydes is that the diacetates formed are quite stable in neutral, acidic, and basic media than the corresponding O,O-acetals.<sup>[1,2]</sup> Diacetates are important precursors in the synthesis of dienes for Diels–Alder reactions.<sup>[1,2,4]</sup>

In presence of acid catalysts, aldehydes react with acetic anhydride to form gem-diacetates. Many reagents are reported in the literature for the synthesis of 1,1-diacetates from aldehydes which include protic acids such as sulfuric and phosphoric acid, Lewis acids like zinc chloride and phosphorous(III) chloride, LiBr, InCl<sub>3</sub>, montmorillonite clay, zeolites, metal triflates, and N-bromosuccinimide.<sup>[5-8]</sup> In view of environmental concern, there is a global effort to replace the conventional catalysts by new solid acids which are easily separable from the products, less toxic, and reusable. Although, zeolites and clays are better alternatives than homogeneous catalysts, they are highly susceptible to deactivation due to pore blocking and hydration. On those lines, promoted metal oxides offer several advantages over zeolites and clay-based catalysts. They are active over a wide range of temperature and more resistant to thermal excursions. Among promoted metal oxide catalysts, sulfate ion doped ZrO<sub>2</sub> exhibits very strong solid acidity and catalyzes many reactions even under very mild conditions.<sup>[9]</sup> However, the sulfated zirconia undergoes rapid deactivation due to loss of sulfate ions during activation and catalytic runs. Recent studies reveal that Mo- or W-oxide doped zirconia also exhibits similar solid acidity and excellent catalytic properies.<sup>[9-14]</sup> It is known that mixed oxides often show enhanced acidity and thermal stability than their constituent single oxides.<sup>[15]</sup> This is primarily due to charge imbalance generated upon the minor component oxide by imposition of the bond matrix of the major component oxide.<sup>[15-17]</sup> Therefore, we undertook investigations to make solid acid catalysts without sulfate ions by extending the mixed oxide analogy to titania-zirconia and other combinations.<sup>[18]</sup> In this communication, we report an efficient and simple methodology for the protection of aldehydes under mild and solvent-free conditions catalyzed by



#### Synthesis of 1,1-Diacetates Using Solid Acid Catalyst

 $Mo/TiO_2-ZrO_2$  solid acid catalyst. The reported method is very useful especially when both ketone and aldehyde groups are present in the same molecule.

The  $Mo/TiO_2$ -ZrO<sub>2</sub> catalyzed synthesis of 1,1-diacetates from various aldehydes and acetic anhydride under solvent-free conditions is summarized in Table 1. As presented in Table 1, aldehydes bearing ring-deactivating groups (electron withdrawing groups) can also be smoothly converted into diacetates in good yields (entries 4 and 5). The  $\alpha$ -,  $\beta$ -unsaturated aldehydes are also converted into diacetates without affecting the double bond (entries 8 and 11). In the case of molecules having both ketone and aldehyde groups, only aldehyde group is selectively converted into diacetate (entry 10). A competitive experiment between benzaldehyde and acetophenone was carried out by taking a mixture of them to confirm the chemoselectivity of the catalyst. Only benzaldehyde was found to convert selectively into diacetate. It can be inferred from this study that the present methodology is highly useful for chemoselective protection of aldehydes from ketones. No appreciable change in the activity of the catalyst was noticed even after four to five cycles. The use of a reusable heterogeneous catalyst in achieving selective protection of carbonyl compounds is very significant from the point of view of its commercial implications.

In conclusion, the present results demonstrate that  $Mo/TiO_2-ZrO_2$  is an efficient catalyst for chemoselective diacetalization of aldehydes under solvent-free conditions. The main advantage of this catalyst is easy operation and simplicity in the work-up, which involves mere filtration of the catalyst and reusability.

#### **EXPERIMENTAL**

#### **Preparation of Catalyst**

The titania–zirconia (1:1 mole ratio) mixed oxide was prepared by a homogeneous coprecipitation method. In a typical experiment, the required quantities of titanium tetrachloride and zirconium oxychloride were dissolved separately in deionized water and mixed together (pH = 2). The resulting solution was neutralized by adding dilute NH<sub>4</sub>OH drop-wise from a burette up to pH 8. The obtained precipitate was washed several times until free from chloride ions and dried at 393 K for 16 hr. To dope molybdenum oxide (10 wt.), the desired quantity of ammonium heptamolybdate was dissolved in excess water and to which the powdered hydrous titania–zirconia mixed oxide was added. The excess water was evaporated on a water-bath with vigorous stirring. The obtained sample was oven dried at 383 K for 12 hr and calcined at 1023 K for

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Entry	Substrate	Product	Yield	Ref.
1	СНО	QAcOAc	94	[5-7]
2	СНО	QAcOAc	91	[5,7]
3	CHO	Cl QAcOAc	89	[5,6]
4	CHO	OCH <sub>3</sub> QAcOAc	92	[5-7]
5	NO <sub>2</sub> CHO NO <sub>2</sub>	NO <sub>2</sub> QAeOAc NO <sub>2</sub>	90	[6]
6	CHO OH	QAcOAc	89	[7]

Table 1. Diacetalization of aldehydes using Mo/TiO<sub>2</sub>-ZrO<sub>2</sub> solid acid catalyst.

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(continued)

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## Synthesis of 1,1-Diacetates Using Solid Acid Catalyst

Table 1. Continued.				
Entry	Substrate	Product	Yield	Ref.
7		OAc	81	[5-7]
8	CH=CH-CH0	CH=CH+OAc	95	[5-7]
9	CHO CH <sub>3</sub>	QAcOAc	96	[5,7]
10	СНО	O OAc OAc	92	[7]
11	сн <sub>3</sub> -сн=сн-сно	$CH_3 - CH = CH \longrightarrow OAc OAc$	79	[5]
12	(CH <sub>3</sub> ) <sub>2</sub> —СН — СНО	$(CH_3)_2$ CH $ CH_{OAc}^{OAc}$	86	[6]
13	CH3	No reaction		

6 hr in air atmosphere. The prepared catalyst was characterized by means of BET surface area, x-ray diffraction, x-ray photoelectron spectroscopy, and Raman techniques.<sup>[18]</sup>

## **General Reaction Procedure**

A mixture of 1:1.5 molar amounts of aldehyde and acetic anhydride along with the catalyst (0.2 g) were taken into a round bottom flask and refluxed at 323 K for 1-2 hr. Completion of the reaction was monitored by



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TLC. After completion of the reaction the catalyst was filtered off. The wet catalyst was used for recycling and no appreciable change in the activity was noted. The product was recovered from the filtrate. An aqueous NaHCO<sub>3</sub> solution was added to remove excess acetic anhydride and  $CH_2Cl_2$  to separate aqueous and organic layers. The organic layer was decanted into another flask by using separating funnel and concentrated. NMR and mass spectrometry techniques were utilized along with their melting/boiling points to analyze the products and GC for quantification.

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