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Natural kaolin supported sulfuric acid as an efficient catalyst for the preparation of 1, 1-diacetates under solvent-free conditions

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ABSTRACT

A facile and efficient method for the preparation of 1,1-diacetates of aldehydes is improved. The acidified kaolin with sulfuric acid (2 % w/w) catalyzed 1,1-diacetates formation from aldehydes in solvent-free conditions. Both aromatic and aliphatic aldehydes gave high yields (85-95 %) of the corresponding 1, 1-diacetates. Advantages of this method are the use of inexpensive and selective catalyst, with high yields in simple operation, and short reaction time under solvent-free conditions.

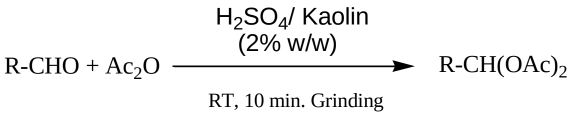
*Key Words****:*** *Aldehydes; 1,1-Diacetates; Kaolin; Protection; Solvent-free.*

1. Introduction

1,1-Diacetates (acylals) are useful protective group for aldehydes [1] and substrates for nucleophilic substitution [2, 3]. They are also important building blocks for the synthesis of dienes for Diels-Alder cycloaddition reaction [4]. Usually, they are synthesized from aldehydes and acetic anhydride using strong proton acids and Lewis acids as catalyst, typically such as sulfuric acid [5], phosphoric acid [6], methanesulfonic acid [6], Nafion-H [7], zinc chloride [8], ferric chloride [9], iodine [10] or phosphorous trichloride [11]. These methods have not been entirely satisfactory, owing to such drawbacks as low yields (4% in the case of 4-nitrobenzaldehyde [11]), long reaction time (up to 120 h in the case of 2-furaldehyde [11]) and tedious work-up. In recent years, β-zeolite [12], sulfated zirconia [13], montmorillonite clays [14], expansive graphite [15], trimethylchlorosilane and sodium iodide [16], scandium triflate [17], N-bromo succinimide [18], PVC-$FeCl_3$ [19], SO_4^{-2}/ TiO_2 [20], SO_4^{-2}/ SnO_2 [21] and heteropolyacids [22, 23] were employed as catalyst for this purpose to obtain relatively better results. Although some of these methods present a convenient procedure with good to high product yields, most of the currently available methods suffer from strong acidic conditions, required high temperature or long reaction time and expensive catalyst loading. Therefore the discovery of a novel mild and catalytic protocol for the efficient conversion of aldehydes into 1,1-diacetates is of general interest.

Natural kaolin is very cheap and shows good potential as support material. Currently, strong interests in such natural supports are due to ecofriendly demands in many modern industrial applications [24]. Kaolin, montmorillonite K10 and KSF supported with transition metal chlorides were employed to esterify tert-butanol with acetic anhydride to tert-butyl acetate with more than 98% selectivity. A noteworthy feature was the low activity of the catalysts for the dehydration of tert-butanol below 50 °C [25]. Thermally activated Nigerian Ukpor kaolinite clay and Udi clay were shown to be good catalysts for the preparation of n-propyl acetate [26]. Brazilian kaolinite intercalated with a porphyrin derivative catalyzed Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactam by hydrogen peroxide. In the presence of the same catalyst iodosylbenzene brings about the epoxidation of cyclooctene and oxidation of cylcohexane to cyclohexanone [27]. Acid-treated clay (K10, bentonite, or kaolin) catalyzed the triazenes formation by diazotization of aryl amines followed by addition of a cyclic secondary amine [28].

In this paper we introduced natural kaolin supported sulfuric acid as an efficient catalyst for the preparation of 1,1-diacetates from aldehydes in solvent-free conditions (Scheme 1).



Scheme 1.

2. Experimental

All materials and solvents were purchased from Merck and Fluka. Melting points were determined in open capillary tubes in an Electrothermal IA 9700 melting point apparatus. ^1H NMR spectra were recorded on a Bruker -100 MHz instrument using tetramethylsilane (*TMS)* as an internal standard. IR spectra were recorded on a Shimadzu-IR 470 spectrophotometer. All of the products are known products and all of the isolated products gave satisfactory IR and NMR spectra.

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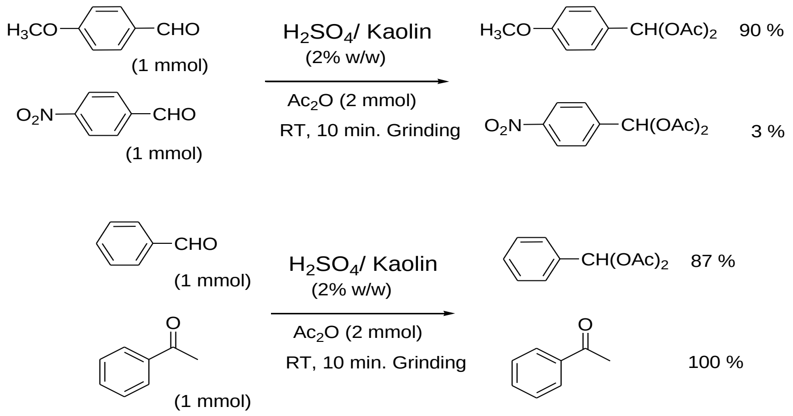


Scheme 2.

2.1. Preparation of the Acidified Kaolin with Sulfuric Acid (2 % w/w).

Kaolin (7.5 g) was treated with concentrated sulfuric acid (0.15 g, 0.08 ml) and stirred for 1h. The prepared acidified kaolin (2 % w/w), was stored for further applications.

2.2. Preparation of 1, 1-Diacetates

Typical procedure: A mixture of benzaldehyde (1.06 g, 10 mmol), acetic anhydride (2.04 g, 20 mmol) and acidified kaolin [2 % w/w, (150 mg)] was ground thoroughly in a mortar for 10 min. The progress of the reaction was monitored by TLC and/or IR spectroscopy (ν_{CO} acylal; 1740-1760 cm^{-1}). After completion of the reaction, dichloromethane (50 mL) was added to the mixture and filtered. The solid material was washed with dichloromethane (2 x 10 mL). The filtrates were combined together and was washed with saturated solution of $NaHCO_3$ and brine and then dried over $MgSO_4$. Removal of the solvent gave the crude product which was subsequently purified by column chromatography (silica gel; eluted with n-hexane / dichloromethane) to afford pure benzaldehyde 1, 1-diacetate in 88 % yield. M.p.: 45-46 ˚C (lit. [11], 44-46 ˚C); IR (KBr); 3060, 1750, 1605, 1475, 1380, 1250, 1200, 1070, 1010, 765 cm^{-1}. ^{1}H-NMR (100 MHz, $CDCl_3$, δ ppm): 7.65 (s, 1H), 7.4-7.8 (m, 5H), 2.2 (s, 6H).

4-Chlorobenzaldehyde-1, 1-diacetate: M.p.: 81-82 ˚C (lit. [23], 81-82 ˚C); IR (KBr); 3060, 1760, 1605, 1470, 1200, 1070, 1010, 780 cm^{-1}. ^{1}H-NMR (100 MHz, $CDCl_3$, δ ppm): 7.55 (s, 1H), 7.2-7.35 (complex AA'BB', 4H), 2.1 (s, 6H).

4-Nitrobenzaldehyde-1, 1-diacetate: M.p.: 125-126 ˚C (lit. [11], 123-125 ˚C); IR (KBr); 3080, 1765, 1605, 1540, 1350, 1200, 1010, 850 cm^{-1}. ^{1}H-NMR (100 MHz, $CDCl_3$, δ ppm): 8.1 (d, 2H, J=9Hz), 7.5 (d, 2H, J=9Hz). 7.5 (s, 1H), 2.05 (s, 6H).

4-Acetoxy-3-methoxybenzaldehyde-1, 1-diacetate: M.p.: 90-91 ˚C (lit.[14b], 90-91 ˚C); IR (KBr); 3060, 1760, 1750, 1610, 1520, 1465, 1380, 1250, 1205, 1160, 1120, 1070, 950, 895, 780 cm^{-1}. ^{1}H-NMR (100 MHz, $CDCl_3$, δ ppm): 8.0 (s, 1H), 7.3-7.7 (m, 3H), 4.2 (s, 3H), 2.5 (s, 3H), 2.3 (s, 6H).

Table 1.

3. Results and Discussion

Clays are nanoparticles with layered structures. The layers possess net negative charge that is neutralized by cations such as Na^+, K^+, Ca^{2+}, etc., which occupy the interlamellar space. The amazing amenability of clays for modification lies in the fact that these interlamellar cations can be very easily replaced by other cations or other molecules. Molecules can be covalently anchored to layer atoms. This provides tremendous scope for altering the properties of clays like acidity, pore size, surface area, polarity and other characteristics that govern their performance as catalysts. Because of these wide ranging possibilities, in addition to their environmental compatibility and cheapness, much effort is expended in discovering newer methods of using clays in their native and modified forms as catalysts for diverse organic reactions.

For this propose we treated natural kaolin with sulfuric acid and examined its capacity for the preparation of 1,1-diacetates from aldehydes. For optimization of the reaction conditions, we have tried the conversion of 4-chlorobenzaldehyde (2 mmol) to the corresponding acylal with acetic anhydride (4 mmol) in the presence of H_2SO_4 /kaolin as catalyst. Various solvents and solvent-free conditions were examined. The yield of the product under solvent-free conditions is higher and reaction time is shorter rather than conventional method. Then, we optimized the amount of catalyst and reaction temperature required for the preparation of acylals. The optimum amount of catalyst was found to be 2 % (w/w) of H_2SO_4 /kaolin under room temperature conditions (Table 1). Reusability of the catalyst is tested by carrying out repeated runs of the reaction on the same batch of the catalyst. After each cycle the catalyst was filtered off, washed with acetone, dried and activated at 120 °C and then reused for successive cycles. It was observed that the activity of acidified kaolin catalyst with sulfuric acid did not decrease even after eight cycles (Table 1).

Therefore, as shown in the Table 2, a series of 1,1-diacetates were synthesized using acidified kaolin with sulfuric acid (2 % w/w) as a catalyst at room temperature under solvent free conditions. Both aromatic and aliphatic aldehydes gave high yields of the corresponding acylals.

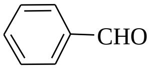
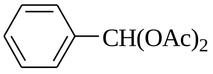
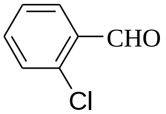
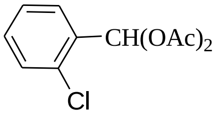
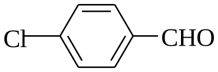
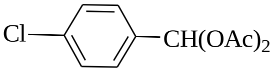
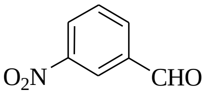
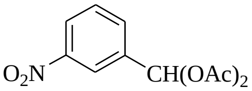
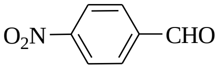
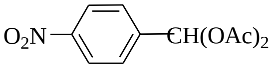
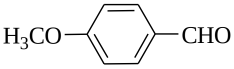
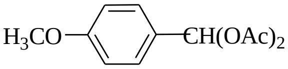
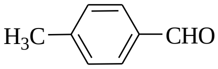
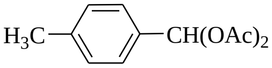
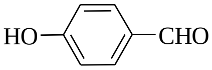
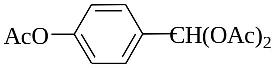
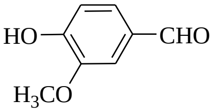
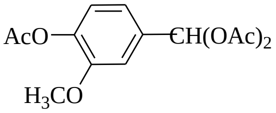
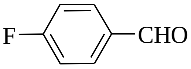
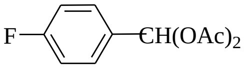
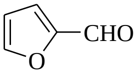
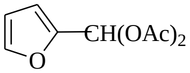
Reaction conditions optimized for conversion of 4-chlorobenzaldehyde to its diacetate in the presence of H_2SO_4 / kaolin (2% w/w) as catalyst and reusability study.

Entry	Solvent	Catalyst (w/w %)	Temperature (°C)	Time (min)	Yield %[a,b]
1	Acetonitril	H_2SO_4 / kaolin 2%	25	240	82
2	Dichloromethane	H_2SO_4 / kaolin 2%	25	240	83
3	Ether	H_2SO_4 / kaolin 2%	25	240	68
4	Toluene	H_2SO_4 / kaolin 2%	25	240	71
5	Cyclohexane	H_2SO_4 / kaolin 2%	25	240	70
6	THF	H_2SO_4 / kaolin 2%	25	240	62
7	Solvent-free	H_2SO_4 / kaolin 2%	25	10	95
8	Solvent-free	H_2SO_4 / kaolin 5%	25	10	95
9	Solvent-free	H_2SO_4 / kaolin 1%	25	10	73
10	Solvent-free	H_2SO_4 / kaolin 1%	50	10	85
11	Solvent-free	H_2SO_4 / kaolin 1%	100	5	94
12[c]	Solvent-free	H_2SO_4 / kaolin 2%	25	10	95
13[d]	Solvent-free	H_2SO_4 / kaolin 2%	25	10	94
14[e]	Solvent-free	H_2SO_4 / kaolin 2%	25	10	93
15[f]	Solvent-free	H_2SO_4 / kaolin 2%	25	10	93
16[g]	Solvent-free	H_2SO_4 / kaolin 2%	25	10	92
17[h]	Solvent-free	H_2SO_4 / kaolin 2%	25	10	90
18[i]	Solvent-free	H_2SO_4 / kaolin 2%	25	10	88

[a] Other conditions: 4-chlorobenzaldehyde (2 mmol), Ac_2O (4mmol), and H_2SO_4 / kaolin (30 mg) as catalyst.
[b] Isolated yields.
[c-i] Reusability of the recovered catalyst in new runs (from run 2 [c] to run 8 [i]).

We were pleased to find that aromatic aldehydes containing electron withdrawing or donor groups gave the corresponding 1,1-diacetates in good to excellent yields in shorter time using acidified kaolin with sulfuric acid (2 % w/w) than some of the reported method. The nature of the substituents on the aromatic ring seems to have no effect on the reaction systems. Moreover, the compounds with sensitive rings (furfural) or functional group (cinnamaldehyde) successfully were converted to corresponding 1,1-diacetates. However, phenol groups were also protected as acetates in hydroxyl containing aromatic aldehydes under these conditions. Whereas literature showed that protection of 4-HO-benzaldehyde was failed [14a] in the presence of montmorillonite K-10 after 48 h, or take place [14b] in the presence of Fe^{+3}-montmorillonite after 8 h, our catalyst improved this reaction by 95% yield in 10 min. Aliphatic as well as α,β-unsaturated aldehydes also produced their corresponding 1,1-diacetates in good yields under the same reaction conditions. It is also worth noting that ketones, such as acetophenone and benzophenone did not give any 1,1-diacetates under the same reaction conditions and this suggested that chemoselective protection of an aldehyde in the presence of a ketone could be achieved. Therefore, to explore the selectivity of this method, we investigated competitive reactions for acylal formation in the mixture of aldehydes and in the mixture of aldehyde and ketone. These reactions proceeded with high selectivity in the presence of this catalyst (Scheme 2).

Table 2.
Preparation of 1, 1-diacetates from aldehydes in the presence of H_2SO_4 / kaolin (2 % w/w).

Entry	Aldehyde	Yield %^{a}	Product^b	m.p / °C	
				Found	Reported [lit.]
1		88		45-46	44-46[11]
2		92		58-59	59 [22]
3		95		81-82	81-82 [23]
4		95		66-67	64-66 [9]
5		89		125-126	123-125 [11]
6		92		63-64	63 [22]
7		94		68-70	68-69 [23]
8		95^c		89-90	89-90 [14b]
9		93^c		90-91	90-91 [14b]
10		89		57-58	58-59 [22]
11		91		53-55	52-54 [12]
12	PhCH=CH-CHO	87	PhCH=CH-CH(OAc)$_2$	85-86	84-86 [23]
13	$CH_3(CH_2)_5$-CHO	85	$CH_3(CH_2)_5$-CH(OAc)$_2$	136	135-136 [29]
14	$CH_3(CH_2)_2$-CHO	88	$CH_3(CH_2)_2$-CH(OAc)$_2$	126	125-128 [6]

[a] Isolated yield.
[b] All compounds give satisfactory spectral analysis (IR and ^{1}H-NMR).
[c] 6 equivalents acetic anhydride were used.

4. Conclusion

In conclusion, we report a mild and efficient catalyst for the preparation of 1,1-diacetates from aldehydes in the presence of the acidified kaolin (2 % w/w) under solvent free conditions. Some advantages of this protocol are: use of inexpensive, non-toxic and reusable catalyst, high yields and selectivity in simple operation, and short reaction times under solvent free conditions. Also, the catalyst is easily prepared and handled from environmentally safe and natural kaolin that means green chemistry.

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