

A Mild and Efficient Method for the Synthesis of Acylals from Aromatic Aldehydes and Their Deprotections Catalyzed by Synthetic Phosphates under Solvent-Free Conditions

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Abstract

An efficient and clean preparation of acylals from aromatic aldehydes in the presence of synthetic phosphates (flourapatite and hydroxyapatite doped with $ZnCl_2$ and $ZnBr_2$) and acetic anhydride was achieved easily in high yields (86% - 97%) at room temperature under solvent-free conditions. Deprotection of the resulting acylals has also been attained by using the same catalysts under microwave irradiation. This method consistently has advantage of excellent yields (82% - 96%) and a short reaction time (3 - 4 min).

Keywords

Synthetic Phosphates, Clean Process, Acylals, Protection, Deprotection

1. Introduction

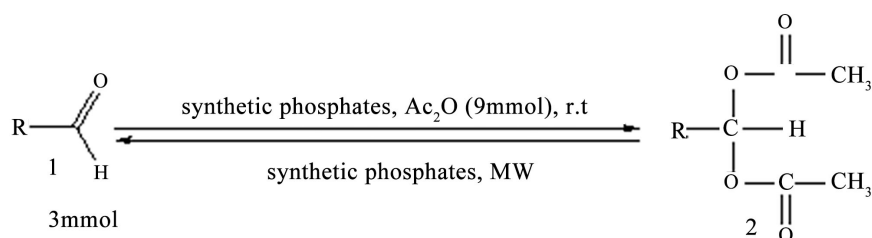
There has been an increasing emphasis among researchers from both academia and industry to design synthetic strategies keeping in view the principles of "Green Chemistry" [1]. Adopting the principles of green chemistry means to reduce or eliminate the generation and use of hazardous substances. In recent years, replacement of hazardous solvents with environmentally benign solvents [2] [3] or development of solvent-free syntheses [4] [5] [6] is one of the major focus areas of Green Chemistry. In other cases, the use of heterogeneous cata-

lysts under solvent-free conditions is becoming very popular as it has many advantages: reduced pollution, reusability, high selectivity, low cost, and simplicity in process and in handling. These factors are especially important in industry.

The 1,1-diacetates (acylals) have been introduced as a suitable protection group for aldehyde because of their remarkable stability to neutral and basic conditions [7]. In addition, they can be converted into other useful functional groups by reaction with appropriate nucleophiles [8] and used as carbonyl surrogates for asymmetric synthesis [9]. 1,1-Diacetates, on the other hand, are ambident substrates containing two types of reactive carbon centres, the carbon atom of the protected aldehyde function and the carbonyl group in the ester moieties [10]. The relative acid stability of 1,1-diacetates is another interesting feature of such 1,1-diacetates in the field of protection-deprotection chemistry [11].

The synthesis of acylals is usually achieved via the reaction of an aldehyde with acetic anhydride (Ac_2O) in the presence of a protic acid [12] [13] [14], Lewis acids [15]-[23], or heterogeneous catalyst [24]-[30]. Many of reported methods, however, involve strongly acidic or oxidizing conditions, corrosive reagents, high temperature, high catalyst loading, longer reaction time and cumbersome procedures. In view of these, the search for finding a cost-effective, mild and simple protocol for synthesis of acylals from aldehydes is still relevant.

In recent years, we have used the synthetic phosphates (hydroxyapatite (HAP) and fluorapatite (FAP)) alone, doped and modified by metal salts as the heterogeneous catalysts for several reactions, such as Knoevenagel condensation [31] [32], Friedel-Crafts alkylation [33] [34] [35], Michael addition [36] [37], hydration of nitriles to amides [38], and Cross aldol Condensation [39]. In this work, we wish to report a mild, convenient and green methodology for the synthesis and deprotection of acylals from aromatic aldehydes using ZnCl_2/FAP , ZnBr_2/FAP , ZnCl_2/HAP and ZnBr_2/HAP .



synthetic phosphates=HAP,FAP,ZnCl₂/FAP ,ZnBr₂/FAP, ZnCl₂/HAP and ZnBr₂ /HAP

2. Results and Discussion

The catalytic activity of the materials prepared has been evaluated in the protection of aromatic aldehydes. First of all, we have tested the apatite (FAP or HAP) alone in the catalysis of the synthesis of acylals (Table 1). The yields obtained are poor. To enhance the activity of apatite (FAP or HAP), the later was doped with different Lewis acids. For an initial evaluation of the activity of $\text{ZnBr}_2/\text{apatite}$

different experiments were carried out using varying values of catalyst weight in the protection of benzaldehyde with acetic anhydride (**Table 1**). The yield of product 2a increased as weight of catalyst increased. This result indicate the positive effect of the catalyst in this transformation, we have chosen 0.1 g of the catalyst for further study.

To explore the scope of this methodology the protection of different substrates was investigated. To appreciate the important enhancement of the activity of the doped materials, we have carried out synthesis of acylals with ZnCl₂/FAP, ZnBr₂/FAP, ZnCl₂/HAP and ZnBr₂/HAP in the same condition (**Table 2**). The positive effect of doped solid catalysts can be observed in all cases. The yields obtained are high (86% - 97%) at room temperature except for the product required relatively longer reaction time (entry 2e) at 70 °C, possibly owing to the strong electron-withdrawing nitro substituent (see **Table 2**). Meanwhile, the presence of electron-donating groups (entry 2b, 2d, 2g, **Table 2**) increases the yields, demonstrating the participation of both the aldehydes and the acetic anhydride in the rate controlling step of the reaction. Furthermore, α , β -unsaturated aldehydes, such as cinnamaldehyde (**Table 2**, product 2f) and acid sensitive aldehydes, such as furfural (**Table 2**, product 2c) reacted well without any decomposition or polymerization under the selected reaction conditions.

To evaluate the influence of the metal halide in the activity of the doped material, we have compared the yields obtained in the synthesis of product 2a using ZnCl₂/HAP, ZnBr₂/HAP, ZnCl₂/FAP and ZnBr₂/FAP. Thus the kinetic curves of these reactions as shown in **Figure 1**, indicate clearly the promoting effect of Lewis acids, ZnBr₂/HAP appear to be somewhat the more active catalyst. Reuse of ZnBr₂/HAP was studied in the synthesis of product 2a. The yields obtained were 94%, 76% and 69% using the fresh catalyst and reused for the first and the second time, respectively. The decrease of the yields can be explained by the accumulation of organic substrates over the active sites of the catalyst.

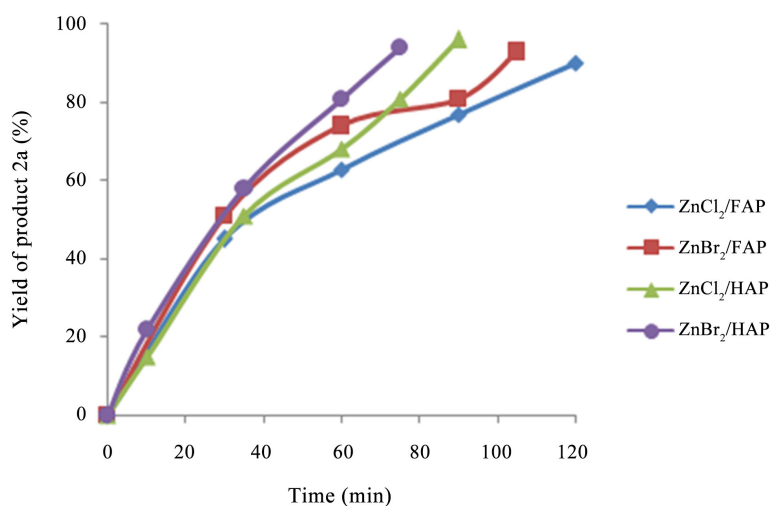
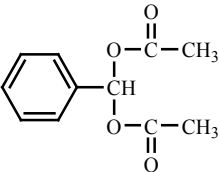
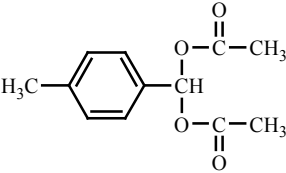
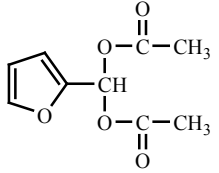
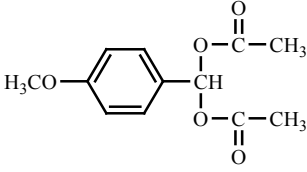
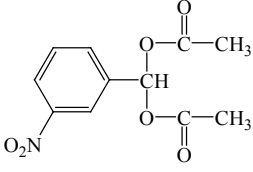
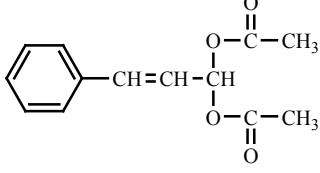
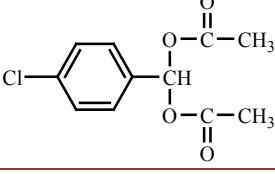


Figure 1. Kinetic curves of product 2a synthesis using HAP and FAP doped with ZnCl₂ and ZnBr₂.

Table 1. Effect of the weight of ZnBr₂/HAP and ZnBr₂/FAP in the synthesis of product 2a.

Weight of catalyst (g)	Catalyst Yield (%) [time (min)]	
	ZnBr ₂ /HAP	ZnBr ₂ /FAP
0.05	53 (75)	56 (105)
0.1	94 (75)	93 (105)
0.2	95 (75)	96 (105)
0.5	95 (75)	96 (105)

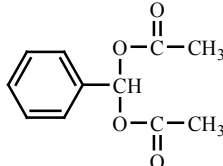
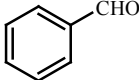
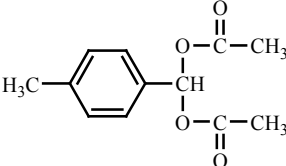
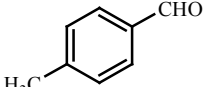
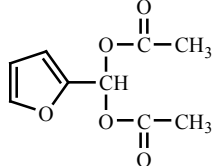
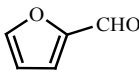
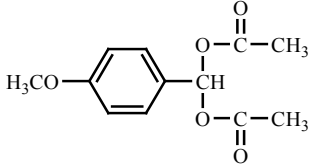
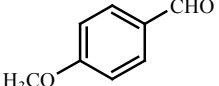
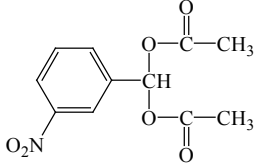
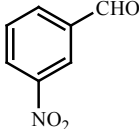
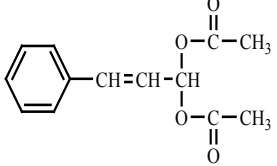
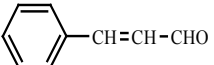
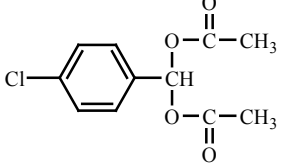
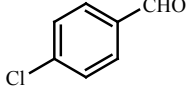
Table 2. Preparation of 1,1-diacetates from aldehydes.

Entry	Product ^a	Catalyst	Yields (%) ^b [time]
2a		HAP	15 (48 h)
		ZnCl ₂ /HAP	96 (90 min)
		ZnBr ₂ /HAP	94 (75 min)
		FAP	11 (48 h)
		ZnCl ₂ /FAP	90 (120 min)
2b		ZnBr ₂ /FAP	93 (105 min)
		HAP	17 (48 h)
		ZnCl ₂ /HAP	97 (90 min)
		ZnBr ₂ /HAP	96 (75 min)
		FAP	16 (48 h)
2c		ZnCl ₂ /FAP	94 (120 min)
		ZnBr ₂ /FAP	95 (105 min)
		HAP	24 (48 h)
		ZnCl ₂ /HAP	90 (20 min)
		ZnBr ₂ /HAP	92 (15 min)
2d		FAP	18 (48 h)
		ZnCl ₂ /FAP	87 (25 min)
		ZnBr ₂ /FAP	92 (25 min)
		HAP	13 (48 h)
		ZnCl ₂ /HAP	93 (40 min)
2e ^c		ZnBr ₂ /HAP	95 (30 min)
		FAP	14 (48 h)
		ZnCl ₂ /FAP	91 (50 min)
		ZnBr ₂ /FAP	89 (45 min)
		HAP	46 (48 h)
2f		ZnCl ₂ /HAP	95 (5 h)
		ZnBr ₂ /HAP	96 (4 h)
		FAP	41 (48 h)
		ZnCl ₂ /FAP	93 (7 h)
		ZnBr ₂ /FAP	96 (6 h)
2g		HAP	19 (48 h)
		ZnCl ₂ /HAP	94 (30 min)
		ZnBr ₂ /HAP	92 (20 min)
		FAP	12 (48 h)
		ZnCl ₂ /FAP	86 (35 min)
		ZnBr ₂ /FAP	91 (35 min)
		HAP	14 (48 h)
		ZnCl ₂ /HAP	90 (40 min)
		ZnBr ₂ /HAP	92 (30 min)
		FAP	9 (48 h)
		ZnCl ₂ /FAP	88 (50 min)
		ZnBr ₂ /FAP	86 (45 min)

^aAll 1,1-diacetates were identified by their ¹H NMR, ¹³C NMR spectra. ^bIsolated yield. ^cThe reaction mixture was stirred at 70 °C.

Recently, microwave-assisted solvent-free synthesis in organic reactions has been of growing interest as an efficient, economic and clean procedure (“green chemistry”) [6] [39] [40] [41] [42]. For these reasons, we have tried the method for deprotection of geminal-diacetates catalyzed by same supports FAP, HAP, ZnBr₂/FAP, ZnCl₂/FAP, ZnBr₂/HAP and ZnCl₂/HAP). The results are summarized in **Table 3**. The reaction were completed within 3 min for

Table 3. Regeneration of aldehydes from 1,1-diacetates.

Entry	Substrate	Product	Catalyst	Yields (%) [time (min)]
2a			HAP	50 (10)
			ZnCl ₂ /HAP	92 (3)
			ZnBr ₂ /HAP	96 (3)
			FAP	48 (10)
			ZnCl ₂ /FAP	91 (4)
			ZnBr ₂ /FAP	93 (4)
2b			HAP	52 (10)
			ZnCl ₂ /HAP	93 (3)
			ZnBr ₂ /HAP	94 (3)
			FAP	46 (10)
			ZnCl ₂ /FAP	86 (4)
			ZnBr ₂ /FAP	91 (4)
2c			HAP	46 (10)
			ZnCl ₂ /HAP	82 (3)
			ZnBr ₂ /HAP	87 (3)
			FAP	42 (10)
			ZnCl ₂ /FAP	74 (4)
			ZnBr ₂ /FAP	77 (4)
2d			HAP	58 (10)
			ZnCl ₂ /HAP	90 (3)
			ZnBr ₂ /HAP	95 (3)
			FAP	44 (10)
			ZnCl ₂ /FAP	90 (4)
			ZnBr ₂ /FAP	92 (4)
2e			HAP	65 (10)
			ZnCl ₂ /HAP	93 (3)
			ZnBr ₂ /HAP	97 (3)
			FAP	49 (10)
			ZnCl ₂ /FAP	92 (4)
			ZnBr ₂ /FAP	94 (4)
2f			HAP	54 (10)
			ZnCl ₂ /HAP	91 (3)
			ZnBr ₂ /HAP	94 (3)
			FAP	41 (10)
			ZnCl ₂ /FAP	88 (4)
			ZnBr ₂ /FAP	93 (4)
2g			HAP	56 (10)
			ZnCl ₂ /HAP	94 (3)
			ZnBr ₂ /HAP	96 (3)
			FAP	46 (10)
			ZnCl ₂ /FAP	89 (4)
			ZnBr ₂ /FAP	90 (4)

ZnX₂/apatite (P = 300 W) and high yields (82% - 96%) of regeneration of aldehydes. Whereas, similar reaction in the presence of apatite alone (P = 500 W) afforded moderate yields of product (49% - 63%) within 10 min of irradiation time.

It was noticed that there was no reaction under microwave without catalyst, and to what was observed in traditional heating without solvent. This shows a certain synergy between catalyst and the microwave. It is thus completely reasonable to think that the effect of the temperature is a determining factor to promote this transformation. Unfortunately, domestic microwave was used and therefore it was impossible to measure the exact temperature during the reaction.

In conclusion, we have developed a clean and easy method for the synthesis of geminal-diacetates from aldehydes in solvent free conditions, and regeneration of aromatic aldehydes from the corresponding acylals in microwave irradiation using metal halides doped apatite (HAP or FAP) as heterogeneous catalysts. The positive effect of doping the apatite with ZnCl₂ and ZnBr₂ has been observed, and the comparison of these materials indicates that ZnBr₂/HAP is the best catalyst for this reaction. The use of metal halides doped apatite offers diverse advantages including simplicity of operation due to the heterogeneous nature of reaction, easy workup and high yields.

3. Experimental

3.1. Preparation and Characterization of the Catalysts

3.1.1. Preparation and Characterization of HAP

The synthesis of hydroxyapatite [33] is carried out by reaction between diammonium phosphate and calcium nitrate in presence of ammonia. An amount of 250 ml of aqueous solutions containing 7.92 g of diammonium phosphate, maintained at a pH greater than 12 by addition of ammonium hydroxide (70 ml), were dropped under constant stirring into 150 ml of a solution containing 23.6 g of calcium nitrate (Ca(NO₃)₂·H₂O). The suspension was refluxed for 4 h. Distilled water (DW) was used to prepare the solutions. The obtained hydroxyapatite was filtered, washed with DW, dried overnight at 80 °C and calcined in air at 800 °C for 1 h before use.

The structure of the obtained hydroxyapatite was confirmed by X-ray diffraction, infrared spectroscopy and chemical analysis. The hydroxyapatite crystallized in the hexagonal system with the space group P6₃/m. The lattice parameters of the prepared HAP are in excellent agreement with standard data: *a* = 6.883 Å and *c* = 9.422 Å. Surface area of the calcined HAP was determined by the BET method from the adsorption-desorption isotherm of nitrogen at its liquid temperature (77 K), and was found to be *S* = 35 m²·g⁻¹.

3.1.2. Preparation and Characterization of FAP

FAP was prepared by the co-precipitation method as previously reported [34]. The structure of the obtained FAP was confirmed by X-ray diffraction, infrared

spectroscopy and chemical analysis. The fluorapatite crystallized in the hexagonal system with the space group P63/m. The lattice parameters of the prepared FAP are in excellent agreement with standard data: $a = 9.364 \text{ \AA}$ and $c = 6.893 \text{ \AA}$. Surface area of the calcined FAP was determined by the BET method, and was found to be $S = 15 \text{ m}^2 \cdot \text{g}^{-1}$.

3.2. Preparation of ZnX_2 /Apatite (ZnX_2 /HAP or ZnX_2 /FAP) [X = Br, Cl]

The preparation of ZnX_2 /apatite was as follows: 10 mmol of ZnX_2 and 10 g of apatite (FAP or HAP) were mixed in 100 mL of water and then evaporated to dryness and dried for 2 h at 150°C before use.

The XRD patterns of ZnX_2 /apatite are similar to that of apatite [34] [35] [36]. The modification of the apatite by ZnX_2 impregnation does not change the crystalline structure of the solid material. The intensity of typical diffraction peaks did not significantly change indicating no disorganization of the crystalline structure of apatite. It should be noted that no ZnX_2 phases were detected on the doped materials in all cases, indicating that ZnX_2 was highly dispersed in the solid apatite.

3.3. Procedure for the Preparation of 1,1-Diacetates

A typical procedure for the preparation of 1,1-diacetates is as follows: the aldehyde (3 mmol) and acetic anhydride (9 mmol) were placed in a two-necked flask with stirring at room temperature. The catalyst (200 mg of apatite (HAP or FAP) or 100 mg of (ZnX_2 /FAP or ZnX_2 /HAP)) was added and obtained mixture was maintained at room temperature (only for entry 2e a temperature at 70°C was needed) for the appropriate time (see **Table 2**). After the completion of the reaction was monitored by TLC (hexane/ethyl acetate 5% - 20%), Et_2O was added to the mixture and filtered, and then the catalyst was again washed with Et_2O and collected for reuse. Evaporation of the solvent followed by column chromatography on silica gel afforded the pure compound corresponding to 1,1-diacetates.

3.4. Procedure for Deprotection of 1,1-Diacetates

A typical procedure for the regeneration of aldehydes from 1,1-diacetates is as follows: 0.5 g of synthetic phosphates were placed, at 500 w for (HAP or FAP) or 350 w for (ZnX_2 /FAP or ZnX_2 /HAP) in a domestic microwave oven, for the appropriate time (**Table 3**). After the completion of the reaction was monitored by TLC (hexane/ethyl acetate 5% - 20%), Et_2O was added to the mixture and filtered. Evaporation of the solvent followed by column chromatography on silica gel afforded the pure compound corresponding to aldehydes.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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