

Article

Facile and Efficient Acetylation of Primary Alcohols and Phenols with Acetic Anhydride Catalyzed by Dried Sodium Bicarbonate

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Abstract: A variety of primary alcohols and phenols were reacted with acetic anhydride at room temperature in the presence of sodium bicarbonate to produce corresponding esters in good to excellent yields. The acetylation of 4-nitrobenzyl alcohol was also carried out using other bicarbonates and carbonates. The reaction in the presence of cesium bicarbonate and lithium carbonate gave 4-nitrobenzyl acetate in excellent yield, while in the presence of Na_2CO_3 , K_2CO_3 , Cs_2CO_3 , or KHCO_3 the yield was in the range of 80%–95%. Calcium carbonate and cobaltous carbonate did not promote the acetylation of 4-nitrobenzyl alcohol using acetic anhydride. The acetylation of 4-nitrobenzyl alcohol was carried out using ethyl acetate, THF, toluene, diethyl ether, dichloromethane and acetonitrile, and gave good yields ranging from 75%–99%. Toluene was the best solvent for the reaction, while diethyl ether was the poorest.

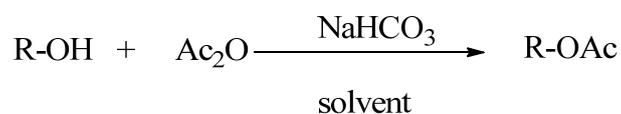
Keywords: carbonates; bicarbonates; acylation; acetic anhydride

1. Introduction

The protection of alcohols and phenols is one of the most frequently employed reactions in organic synthesis and is normally achieved by acylation with anhydrides or acyl chlorides in the presence of tertiary amine bases such as either triethylamine or pyridine [1,2]; Lewis or protonic acids [3–11]; or sometimes solid acid catalysts [12–14]. The rate of acetylation in the basic conditions is known to be raised multifold if 4-(dimethylamino)pyridine (DMAP) is used as a cocatalyst [15,16]. Tributyl

phosphine was introduced as a less basic catalyst than amines in the acetylation of alcohols [17,18]. In recent years, it has been shown that several metal triflates such as $\text{In}(\text{OTf})_3$ [19], $\text{Cu}(\text{OTf})_2$ [4], $\text{Bi}(\text{OTf})_3$ [20], $\text{ZrO}(\text{OTf})_2$ [21], $\text{Ce}(\text{OTf})_4$ [22], $\text{Gd}(\text{OTf})_3$ [23], and $\text{Sc}(\text{OTf})_3$ [24–28], as well as Me_3SiOTf [29,30] are excellent catalysts for efficient acetylation of various types of structurally diverse alcohols with acetic anhydride. Other metal salts such as $\text{TiCl}_4\text{-AgClO}_4$ [31], LiClO_4 [32], CoCl_2 [11], and $\text{Mg}(\text{ClO}_4)_2$ [33] have also been successfully used. In 2004, Phukan used iodine as a catalyst for the acetylation of alcohols under solvent-free conditions [34]. There have also been reports on the acylation of alcohols using acetic anhydride, catalyzed by silica gel supported $\text{Ce}(\text{SO}_4)_2$, $\text{Ti}(\text{SO}_4)_2$, $\text{Fe}_2(\text{SO}_4)_3$, and NaHSO_4 [35]. Although the majority of these methods ensure good results, there is still a great need for simple, mild, less toxic and easy-to-handle catalysts to generate esters. Some of the reported methods for the acetylation of alcohols suffer from one or more disadvantage such as toxicity, cost, drastic reaction conditions, hygroscopicity, thermal stability, and explosiveness of reagents. Pyridine is a popular catalyst for the acetylation of alcohols using acetic anhydride, but is toxic, has a bad smell, and its high boiling point makes its removal after the reaction difficult. Pyridine is normally used in excess and because of its high boiling point its removal is difficult and can complicate product isolation if very small amount of ester has been synthesized. Given those drawbacks, new, efficient, and eco-friendly methods are still in demand. In search for simpler catalysts and our interest in coming up with new acylation methodology, we started screening metal carbonates and bicarbonate as possible mild bases for the anhydride-mediated acylation of alcohols and phenols. Singh reported the chemoselective esterification of phenolic acids in the presence of sodium bicarbonate in ionic liquids using dialkyl halides and sulfates [36]. Solid potassium carbonate has also been used for the selective acetylation of primary alcohols using ethyl acetate via a transesterification process [37,38], but no direct methods using either carbonates or bicarbonates to acetylate alcohols using acetic anhydride have been reported. In this paper, we wish to report a new, mild, and efficient protocol for acetylation of alcohols and phenols using acetic anhydrides in the presence of bicarbonate (Scheme 1).

Scheme 1. Reaction of an alcohol with acetic anhydride in the presence of sodium bicarbonate.



2. Results and Discussion

We first examined the acetylation of 4-nitrobenzyl alcohol using a large excess of Ac_2O in the presence of a large excess of previously dried NaHCO_3 in dry ethyl acetate at room temperature. The reaction proceeded with high efficiency. After many trials, we found out that it took Ac_2O (5 equiv.) and NaHCO_3 (2 equiv.) to obtain good yield of 4-nitrobenzyl acetate (Scheme 2). More Ac_2O and NaHCO_3 did not improve the yield. Using less of any of those two reagents resulted in lower amount of product (data not shown). Next we screened other bicarbonates and carbonates using similar conditions. As shown in Table 1, sodium bicarbonate, cesium bicarbonate and lithium carbonate promoted the acetylation of 4-nitrobenzyl alcohol more efficiently than other carbonates and bicarbonates. The results also indicate

that there is no correlation between Group I metal ionic size and the catalytic activity of carbonates or bicarbonates.

Scheme 2. Acetylation of 4-nitrobenzyl alcohol using acetic anhydride in the presence of sodium bicarbonate as a catalyst.

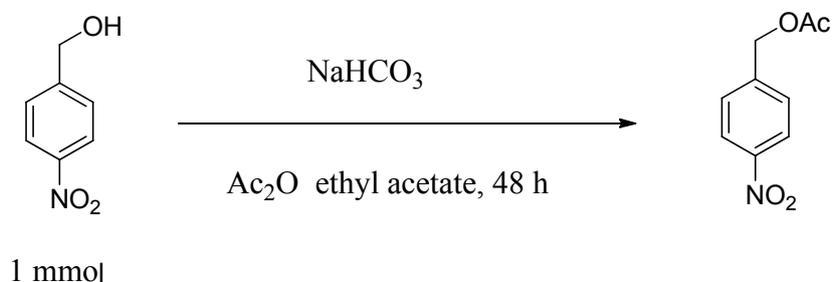


Table 1. Carbonate- and bicarbonate-catalyzed acetylation of 4-nitrobenzyl alcohol.

Bicarbonate ^a	Yield (%)
None	45
NaHCO ₃	95
KHCO ₃	80
CsHCO ₃	>99
Li ₂ CO ₃	>99
Na ₂ CO ₃	90
K ₂ CO ₃	92
Cs ₂ CO ₃	85
CaCO ₃	42
CoCO ₃	45

^a Reaction conditions: 4-nitrobenzyl alcohol (1 mmol), carbonate or bicarbonate (2 equiv.), Ac₂O (5 equiv.), ethyl acetate (6 mL), room temperature, 24 h.

The amount of 4-nitrobenzyl acetate formed in the presence of cobaltous carbonate and calcium carbonate was the same as in the absence of a catalyst, indicating that those two carbonates did not promote the acetylation of 4-nitrobenzyl alcohol. The failure of calcium carbonate and cobaltous carbonate to promote the acetylation is probably due to the insolubility of the carbonates in the trace amount of water present in ethyl acetate. In order to promote the acetylation, bicarbonate and carbonate ions are generated, and the ionization requires water.

Yan Xiong and Mallesha *et al.* [37,38] demonstrated that heterogeneous carbonates were capable of catalyzing the acetylation of alcohol via a transesterification process. Both authors used ethyl acetate and carbonates at high temperature for the reaction. In order to rule out the possibility of transesterification during sodium bicarbonate- promoted acetylation of 4-nitrobenzyl alcohol in the presence of acetic anhydride at room temperature, the reaction was run using other solvents. As shown in Table 2, the reaction was most efficient in toluene, giving greater than 99% yield. The reaction in ethyl acetate gave 93% yield after 24 h. Acetylation in acetonitrile or in dichloromethane required longer reaction time of 48 h to produce 90% in acetonitrile and 85% yield in dichloromethane. When THF was used as a solvent, a solid mass that was difficult to stir using a magnet stirrer was formed.

More solvent (3 mL) was added after 16 h, and the reaction mixture stirred for another 8 h to produce 90% yield of the product. The reaction in diethyl ether was the least efficient, yielding only 75% of the product after 48 h. When the reaction was carried out in diethyl ether that was re-distilled using sodium wire, only 61% of product was obtained. This is probably due to very little ionization of sodium bicarbonate in anhydrous ether.

Table 2. Acetylation of 4-nitrobenzyl alcohol using different solvents.

Solvent (6 mL)	Time (h)	Yield (%)
Ethyl acetate	24	93
THF ^a	24	90
Toluene	24	>99
Diethyl ether	48	75
Anhydrous diethyl ether	48	61
Dichloromethane	48	85
Acetonitrile	48	90

^a9 mL of THF.

In order to probe the effect of water on the acetylation of alcohols using sodium bicarbonate as catalyst, known amounts of water were added to the reaction mixture (Table3). The reaction mixture consisted of p-nitrobenzyl alcohol (0.153 g, 1 mmol), Ac₂O (0.035 g, 5 mmol), NaHCO₃ (0.21 g, 2 mmol) and different amount of water, ranging from 0.5 mmol to 3 mmol. As more water was added, the amount of ester produced decreased, indicating that water is probably competing with the alcohol for the reaction with acetic anhydride to produce acetic acid. The best yield was obtained in the absence of any added water.

Table 3. Effect of the amount of water on the acetylation of 4-nitrobenzyl alcohol in ethyl acetate.

Entry	Amount of water (μL)	Yield (%)
1	No water added	95
2	9	89
3	18	85
4	36	77
5	54	80

Table 4 shows the overall applicability of sodium bicarbonate as a promoter of acetylation of alcohols and phenols. The majority of the reactions went to completion after 24 h. In some solvents, the reaction required 48 h to form products in good yield. The reaction of secondary alcohols entry 4 and 9 required heat. After one hour in boiling toluene the corresponding products, 1-phenylethyl acetate and cyclohexyl acetate were isolated in 90% and 87% yield, respectively. Betulin which has contains both primary and secondary alcohol groups also produced betulin diacetate in 90% after refluxing for one hour in toluene. Reaction at room temperature in different solvents produced a mixture of products. A secondary alcohol is a little bit more hindered than a primary alcohol and as

such, the initial attack of acetic anhydride to produce the intermediate has a higher energy barrier, slowing down the reaction rate.

Table 4. Acetylation of alcohols and phenols.

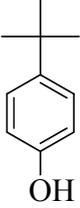
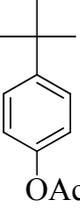
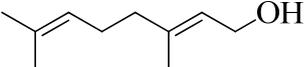
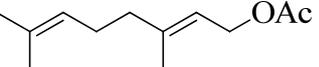
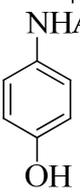
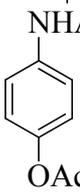
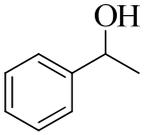
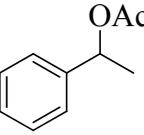
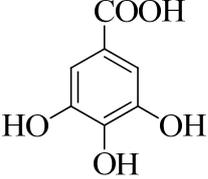
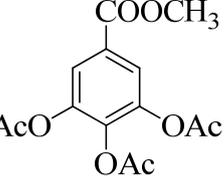
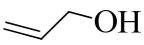
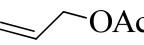
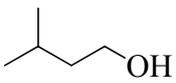
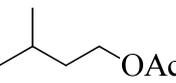
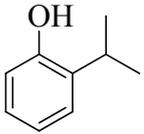
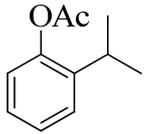
Entry	Alcohol or phenol in 6 mL of solvent ^a	Product	Ref. ^h	Yield (%)
1			[39]	>99
2			-	90 ^b
3			[40]	95
4				90 ^{b,c}
5			[41]	>99 ^d
6				95 ^b
7				88 ^b
8			[40]	92

Table 4. Cont.

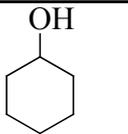
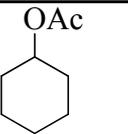
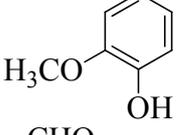
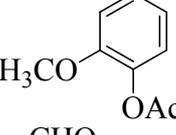
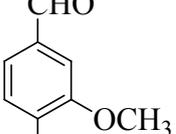
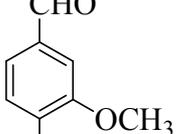
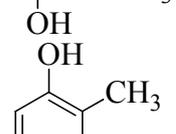
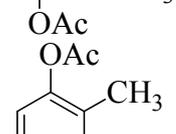
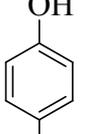
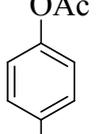
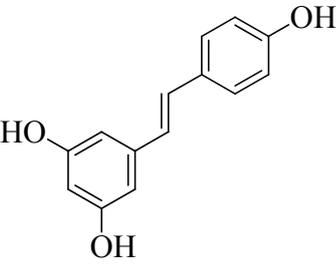
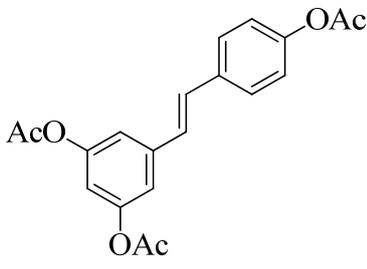
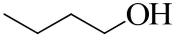
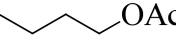
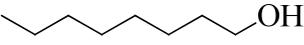
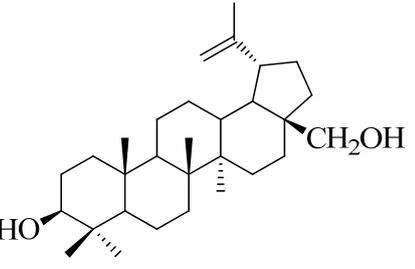
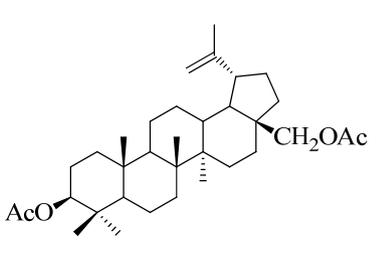
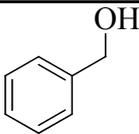
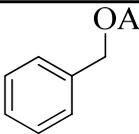
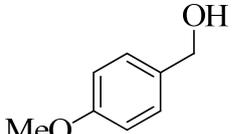
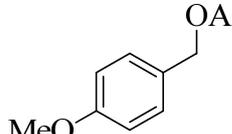
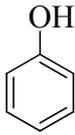
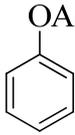
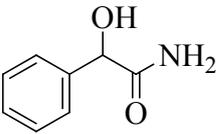
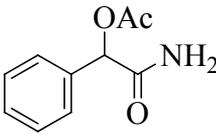
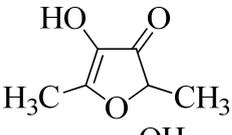
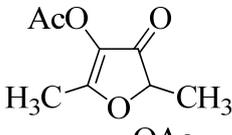
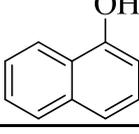
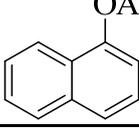
9			-	87 ^{b,c}
10			[42]	80
11			[43]	>99
12			[39,40]	90
13			[40,44]	>99
14			[45]	95 ^d
15			-	93 ^b
16			-	95 ^b
17			[46,47]	90 ^e

Table 4. Cont.

18			[41,44]	>99
19			[39,40]	95
20			-	91 ^b
21			[48]	83 ^{f,g}
22			[49]	82 ^g
23			[39,44]	92 ^f

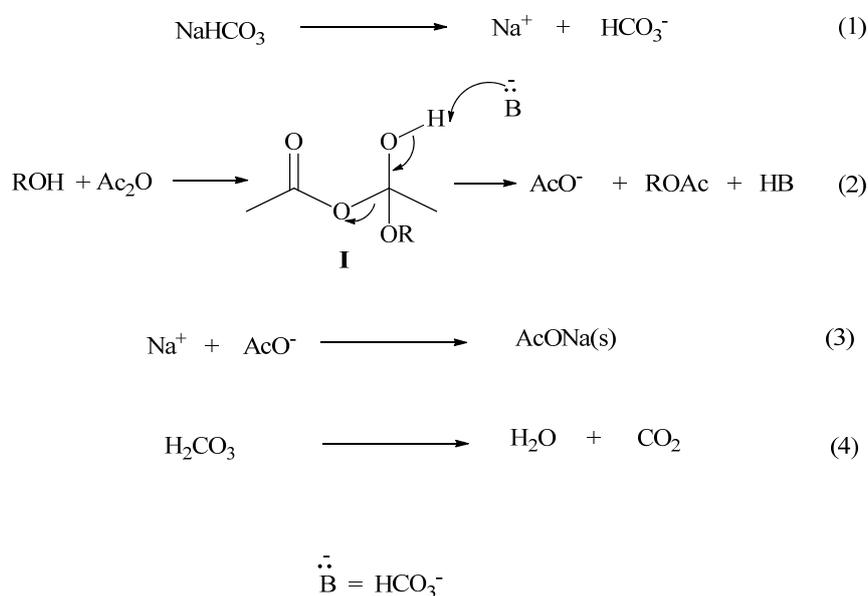
^a 1 mmol of alcohol, NaHCO₃ (2 equiv.), Ac₂O (5 equiv.) in toluene at room temperature. ^b GC yield. ^c In toluene at 110 °C. ^d NaHCO₃ (6 equiv.), Ac₂O (15 equiv.). ^e NaHCO₃ (4 equiv.), Ac₂O (10 equiv.). ^f Solvent system: Acetonitrile (4 mL), ethyl acetate (2 mL). ^g 48 h; all others took 24 h; ^h ¹H-NMR of products.

Phenols with some steric hindrance, entries 8, 10, 11, 12, and 21 gave acetate with 80%–99% yield. Also the reaction proceeded well in the presence of an amide functional group, entries 3 and 21.

Mechanism

A small amount of sodium bicarbonate dissociates (Equation 1, Scheme 3). Nucleophilic attack of the alcohol on acetic anhydride produces intermediate I. The bicarbonate ion abstracts a proton from the intermediate to form carbonic acid, and the rest of the intermediate breaks down simultaneously releasing AcO⁻ and ROAc. The acetate and sodium ions combine to form sodium acetate, which is insoluble in the mixture and forms a white precipitate (Equation 3). The carbonic acid decomposes to produce carbon dioxide and water (Equation 4). The water formed dissolves more sodium bicarbonate, which initiates another cycle of reaction as the catalyst gets consumed. The reaction of 4-nitrobenzyl alcohol (1 mmol), NaHCO₃ (2 equiv.), Ac₂O (5 equiv.), plus crushed dry 3 Å molecular sieves (0.1 g) in toluene was somewhat inhibited (data not shown), indicating that the presence of traces of water in the organic solvent is needed for the acylation to take place. Moreover, when anhydrous ether was used as solvent, the efficiency of the catalyst was reduced. The sparingly soluble carbonates, CaCO₃ and CoCO₃ did not promote the reaction.

Scheme 3. Mechanism of the sodium bicarbonate catalyzed acetylation of an alcohol using acetic anhydride.



3. Experimental Section—General Procedure

All solvents used for acetylation were dried for one week, using previously activated (90 °C) 3 Å molecular sieves. Salts were dried to constant weight in an oven at 90 °C. Product identification was carried out using NMR and GC. NMR data were consistent with those previously reported. In a typical run, a mixture of 4-nitrobenzyl alcohol (0.153 g, 1 mmol), Ac₂O (0.035 g, 5 mmol), NaHCO₃ (0.21 g, 2 mmol), and solvent (6 mL) was stirred at room temperature for the 24 h. The progress of the reaction was followed by TLC. After completion of the reaction, the mixture was filtered and the filtrate was concentrated. To the residue was added dichloromethane (15 mL) and water (5 mL) and the phases separated. The organic phase was dried (Na₂SO₄) and concentrated. The syrup was crystallized from a mixture of hexane and ethyl acetate to give the pure product. Liquid products were cleaned after extraction by passing them through a short silica gel column, eluting with a 50:50 (v/v) mixture of ethyl acetate and a hexane. Carbon dioxide was detected using lime water. Solid sodium acetate was converted to acetic acid, which was analyzed using IR.

4. Conclusions

A new method for the acetylation of primary alcohols and phenols has been developed and can supplement the many other protocols that are available. The reaction of alcohols and phenols with acetic anhydride in the presence of sodium bicarbonate is easy to carry out and gives acetates efficiently. Being able to carry out the acylation in different solvents makes the reaction more versatile. Excellent yields, cheap and readily available reagents, and easy work-up are the advantages of the present method.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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