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Acetylation of Alcohols, Amines, Phenols, Thiols under Catalyst and Solvent-Free Conditions

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Abstract: In the present study, an easy and an efficient approach is reported for the acetylation of alcohols, amines, phenols, and thiols under solvent- and catalyst-free conditions. The experimental conditions were milder than conventional methods and the reactions were completed in shorter reaction time. The examined substrates afforded higher yields of the acetylated products under the short reaction time. Comparison of this work with earlier reported procedures reveals that this method offers some advantages than with reported catalysts and solvents. The as-synthesized products were characterized by ^{1}H-NMR and GC-MS techniques to ensure their purity and identity. In addition, a possible mechanism was also proposed for this reaction.

Keywords: acetylation; phenol; amines; green chemistry; solvent-free; catalyst-free

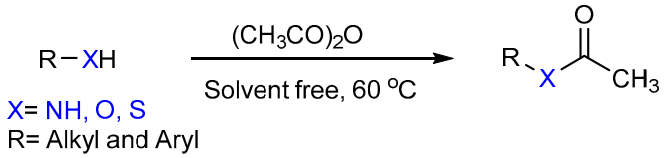
1. Introduction

Acetylation is one of the most important reactions in organic synthesis because acetyl groups can be conveniently used to protect a wide range of functional groups including alcohols, amines, phenols, and thiols, among others [1,2]. Acetylation with acyl halides or acid anhydrides has been reported using either homogeneous or heterogeneous acid catalysts [3–12] or base catalysts [13–17]. Subsequently, a wide range of homogeneous transition-metal-based or organocatalysts have been developed for the acetylation of alcohols using $RuCl_3$ [18], $CeCl_3$ [19], $ZrCl_4$ [20], $La(NO_3)\cdot 6H_2O$ [21], $Al(OTf)_3$ [22], AgOTf [23], Co(II)salen-complex [24], $NiCl_2$ [25], $CoCl_2$ [26], iodine [27], $Ph_3P^+CH_2COMeBr^-$ [28], Cp_2ZrCl_2 [29], $Mg(NTf_2)_2$ [30], $H_3[P(Mo_3O_{10})_4]\cdot nH_2O$ [31], 3-nitrobenzeneboronic acid [32], (4-dimethylaminopyridine) [33], (4-(*N*,*N*′-dimethylamino)pyridine hydrochloride) [34], $CuZr(PO_4)_2$ NPs [35], melamine trisulfonic acid [36], tin(IV)porphyrin-hexamolybdate [37], and $NaOAc\cdot 3H_2O$ [38]. Furthermore, acetylation has also been reported with a series of heterogeneous catalysts, such as ionic liquids [39], ZnO [40,41], CuO-ZnO [42], nano γ-Fe_2O_3 [43], Fe_3O_4@PDA-SO_3H [44], polymer-supported $Gd(OTf)_3$ [45], silica-sulfamic acid [46], borated zirconia [47], $ZnAl_2O_4$ [48], P_2O_5/Al_2O_3 [49], poly(*N*-vinylimidazole) [50], CMK-5-SO_3H [51], 4-dimethylaminopyridine-microporous organic nanotube networks [52], maghemite-ZnO [53], and graphene-grafted *N*-methyl-4-pyridinamine [54]. These methods exhibit some obvious advantages like low reaction temperature, higher conversions of substrates at short reaction time, and the ability of heterogeneous catalysts to be recycled. On the other hand, some of these reported methods use either acid or base, metal salts, and metal nanoparticles, thus experiencing some limitations in the work-up procedure and purification process.

Nardi and co-workers have reported sustainable methods for the protection of functional groups which include $Er(OTf)_3$ as an environmentally benign catalyst for the protection and derivatization of biomolecules [55], derivatization of functional groups employing aqueous microwave-assisted conditions [56] and a simple and an efficient method for the removal of Fmoc in an ionic liquid [57].

In contrast to these reports, Ranu and co-workers have developed a simple and efficient method for the acetylation of alcohols, amines, and thiols with acetic anhydride or acetyl chloride under solvent- and catalyst-free conditions under nitrogen atmosphere at 80–85 °C [58]. However, this method possesses some limitations, including the requirement of high reaction temperature (80–85 °C), the need of inert atmosphere throughout the reaction time, and incomplete conversion of some substrates under the optimized reaction conditions.

Therefore, there is a space to develop an efficient protocol for the acetylation reaction involving solvent and catalyst-free conditions under mild reaction temperature. Hence, the present work aims to provide an alternative method to the previously reported procedures by developing a simple and efficient method for the acetylation of alcohols, amines, phenols, and thiols using acetic anhydride (Scheme 1) under solvent- and catalyst-free conditions. This method provides complete conversion of substrates with very high selectivity of the desired products at moderate reaction temperature under air atmosphere. The optimized reaction conditions are further extended to synthesize a series of acetylated derivatives with very high yields.



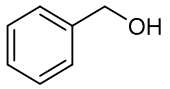
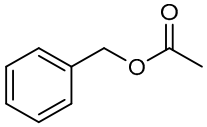
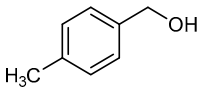
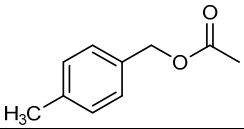
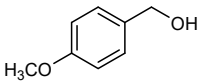
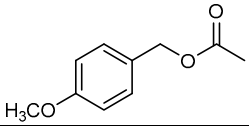
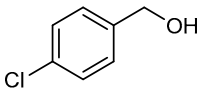
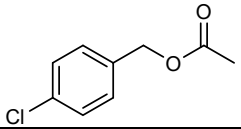
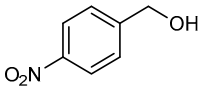
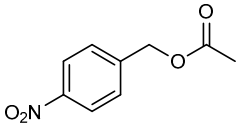
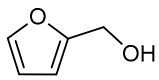
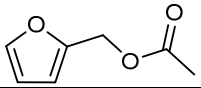
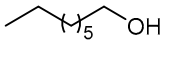
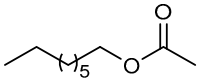
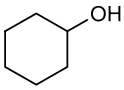
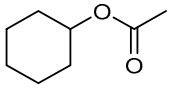
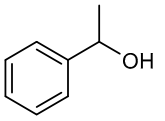
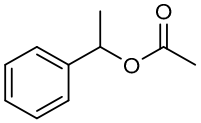
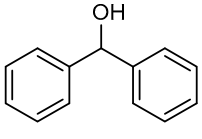
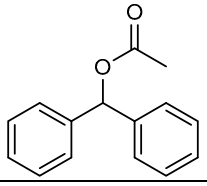
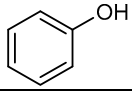
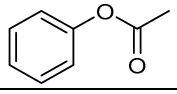
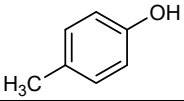
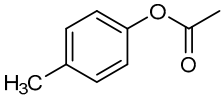
Scheme 1. Acetylation of alcohols, phenols, thiols, and amines under catalyst and solvent-free conditions.

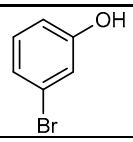
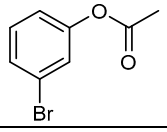
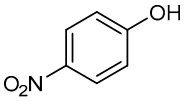
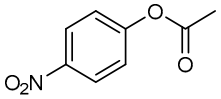
2. Results

In the initial stage of our investigation, benzyl alcohol was selected as a model substrate to optimize the reaction conditions. The observed results are presented in Table 1. The acetylation of benzyl alcohol with acetic anhydride gave 63% conversion with 100% selectivity of benzyl acetate after 24 h at room temperature (Table 1, entry 1). Interestingly, complete conversion of benzyl alcohol with 100% selectivity to benzyl acetate was achieved at 60 °C after 7 h (Table 1, entry 1). The benzyl alcohol conversion was only 88% when the reaction mixture was stirred magnetically under identical conditions (Table 1, entry 1). Therefore, further experiments were carried out at moderate temperature (60 °C) without magnetic stirring to accomplish complete conversion of substituted benzyl alcohols within a short reaction time. With these optimized conditions in hand, a series of benzyl alcohols with electron-donating and electron-withdrawing substituents were examined and achieved more than 99% conversions with 100% selectivities of the corresponding acetylated products after 8 h (Table 1, entries 2–4). However, 4-nitrobenzyl alcohol provided quantitative conversion with 100% selectivity after 12 h under identical conditions (Table 1, entry 5). Furthermore, a heterocyclic alcohol like furfuryl alcohol gave complete conversion and selectivity after 7 h (Table 1, entry 6). On the other hand, the aliphatic and alicyclic alcohols like 1-octanol and cyclohexanol furnished quantitative conversions to their respective esters with high selectivities after 7 and 8 h, respectively (Table 1, entries 7 and 8). Moreover, sterically crowded substrates like 1-phenylethanol and diphenylmethanol afforded more than 99% and 98% conversions, respectively, after 20 h (Table 1, entries 9 and 10). Furthermore, the substrate scope was further expanded to generalize this method by examining phenols and their derivatives under identical conditions. Phenol exhibited quantitative conversion with complete selectivity towards phenylacetate after 12 h (Table 1, entry 11). Substituted phenols such as 4-methyl-, 3-bromo- and 4-nitrophenols resulted in more than 99% conversions to their corresponding esters after 20 h (Table 1, entries 12–14). In addition, α- and β-naphthols showed more than 98% and 99% conversions, respectively, to their corresponding esters after 20 h (Table 1, entries 15 and 16). In general, the observed data under the present experimental conditions show that phenols reacted comparatively slower than alcohols, and this may be due to the reduced nucleophilic character of phenols. Similarly, the feasibility of this methodology was further expanded to aromatic and alicyclic amines. Interestingly, aniline and its derivatives were converted to their respective acetylated products in higher yields within 30 min

(Table 1, entries 17–21). Finally, this method was also extended to study the reactivity of thiols, and the observed results are given in Table 1. These data indicate that thiophenol and its substituted analogues provided higher yields under identical reaction conditions (Table 1, entries 22–24).

Table 1. Acetylation of alcohols, phenols, amines, and thiols under catalyst- and solvent-free conditions. [a]

Entry	Substrate	Product	Time (h)	Conv. [b] (%)	Sel. [b] (%)	Isolated Yield (%)
1			24	63 [c]	100	60
			7	100	100	98
			7	88 [d]	100	82
2			8	>99	100	96
3			8	>99	100	96
4			8	>99	100	96
5			12	>99	100	95
			16	>99 [f]	100	96
6			7	100	100	97
7			7	100	100	98
8			8	>99	100	96
9			20	>99 [e]	100	95
10			20	>98 [e]	100	95
11			12	>99 [e]	100	96
12			20	>99	100	95

13			20	>99	100	97
14			20	99	100	96
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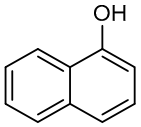
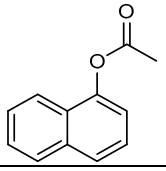
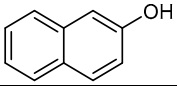
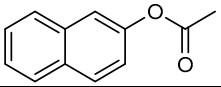
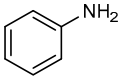
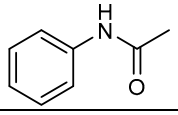
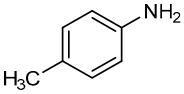
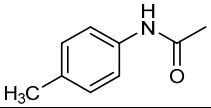
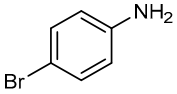
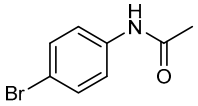
15			20	>98	100	95
16			20	>99 [e]	100	98
17			0.5	100	100	97
18			0.5	100	100	98
19			0.5	100	100	98
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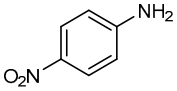
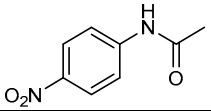
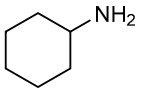
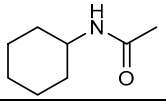
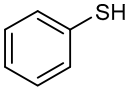
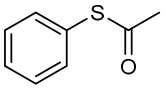
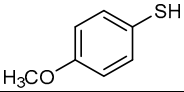
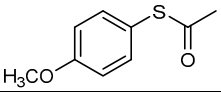
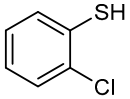
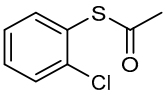
20			0.5	100	100	97
21			0.5	100	100	96
22			4	100	98	94
			15	99 [e,f]	98	96
23			6	100	97	95
24			20	86 [e]	97	80

[a] Reaction conditions: Substrate (1 mmol), acetic anhydride (1.5 mmol), 60 °C; [b] Conversion and selectivity were determined by GC; [c] At room temperature; [d] Performed with stirring; [e] At 70 °C; [f] Reaction conditions: Substrate (10 mmol), acetic anhydride (15 mmol), 60 °C.

3. Discussion

In order to illustrate some benefits of this method, the observed results were compared with previous reports using homogeneous and heterogeneous catalysts, and they are shown in Table 2. These comparisons reveal that the present work offers many advantages, such as short reaction time, minimal use of acetic anhydride, and the achievement of higher yields in the absence of catalyst and solvent. Furthermore, it is interesting to note that the present experimental conditions could provide catalytic results comparable to those data either with homogeneous or heterogeneous catalysts.

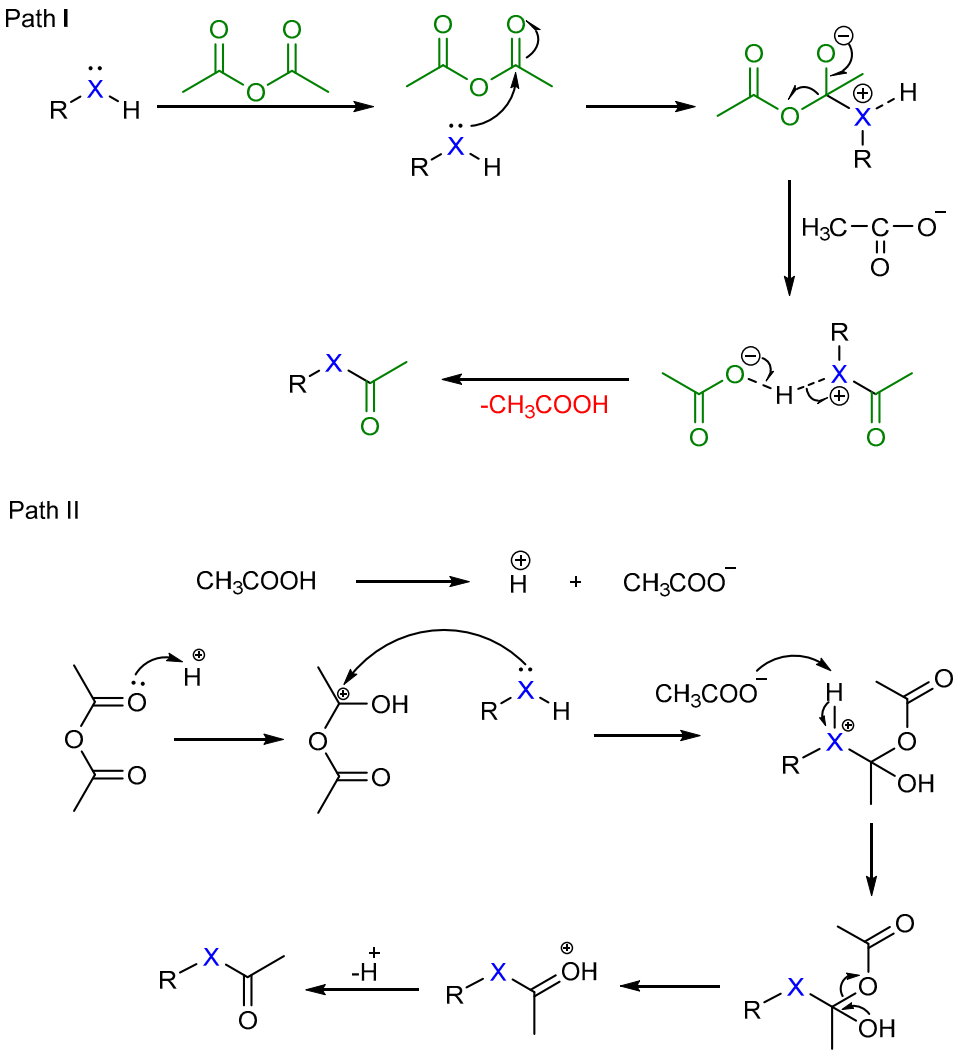
Therefore, the method in this work can be considered as an alternative method for acetylation reaction from a green chemistry perspective.

Table 2. Comparison of the present catalytic data with literature reports for the acetylation reaction.

Entry	Substrate (mmol)	$(CH_3CO)_2O$ (mmol)	Catalyst	Solvent	T (°C)	Time (h)	Ref.
1	1	2	$Cu(OTf)_2$	DCM	RT	2	[11]
2	1	1.2	$RuCl_3$	CH_3CN	RT	10 min–72 h	[18]
3	1	1.5–2	$Ph_3P^+CH_2COMeBr^-$	-	RT	0.5–3.5	[28]
4	55.5	83	$Gd(OTf)_3$	CH_3CN	25	5 min–14 h	[59]
5	1	5	Co(II)salen-complex	-	50	0.5–2	[24]
6	5	6	$CoCl_2$	-	RT	10–50 min	[26]
7	1	1.1	$NaOAc{\cdot}3H_2O$	-	RT	10 min	[38]
8	10	11	DMAP·HCl	Toluene	RT-110	4–28	[34]
9	0.1	0.15	DMAP-MONN [a]	CH_2Cl_2	RT	0.5–5	[52]
10	6.9	7.6	Maghemite-ZnO	-	RT	3	[53]
11	1	1.5	G-NMPA [a]	-	35	2–10	[54]
12	0.5	0.55	CBr_4	-	60	3–6	[60]
13	2.5	2.5	$InCl_3$	-	RT	30 min	[61]
14	2	4	Cu(BDC)	-	RT	24	[62]
15	1	1.5	$H_{14}[NaP_5W_{30}O_{110}]$	-	RT	0.5–3	[63]
16	2	4–20	$LiClO_4$	-	25–40	4–48	[64]
17	1	1.5	-	-	60–70	7–20	Present work

[a] Additionally 1.5 equivalent triethylamine was used.

Based on the observed results in Table 1, a suitable mechanism is proposed for the acetylation of alcohols, phenols, and amines (Scheme 2). The lone pair of electrons on oxygen and nitrogen attack the carbonyl group in acetic anhydride to give an adduct which later eliminates acetic acid to give the corresponding ester (Path I). Furthermore, the liberated acetic acid can also participate in this mechanism. Initially, acetic acid protonates the carbonyl group of acetic anhydride to give a cationic intermediate which is further attacked by the nucleophile to give an alcohol-type intermediate. Later, this intermediate undergoes a series of steps including electron migration to eliminate acetic acid followed by the removal of a proton to give the final desired product (Path II).



Scheme 2. A plausible mechanism for the acetylation of alcohols, amines, phenols, and thiols under catalyst- and solvent-free conditions.

In order to demonstrate the feasibility of this method in a gram-scale synthesis, a series of experiments were performed at a gram scale under identical conditions, and the observed data are shown in Table 1 and Figure 1. It is clearly evident that the present method afforded quantitative yields of 4-nitrobenzylacetate, 4-bromoacetanilide, and 4-nitrophenylacetate from 4-nitrobenzyl alcohol, 4-bromoaniline, and 4-nitrophenol, respectively, under the optimized conditions as shown in Table 1. One of the main advantages of this method is the isolation of the desired products without column chromatography purification, and it can be readily scaled up without any difficulty. Figure 1 shows the isolated products of 4-nitrobenzylacetate, 4-bromoacetanilide, and 4-nitrophenylacetate in a gram-scale synthesis.

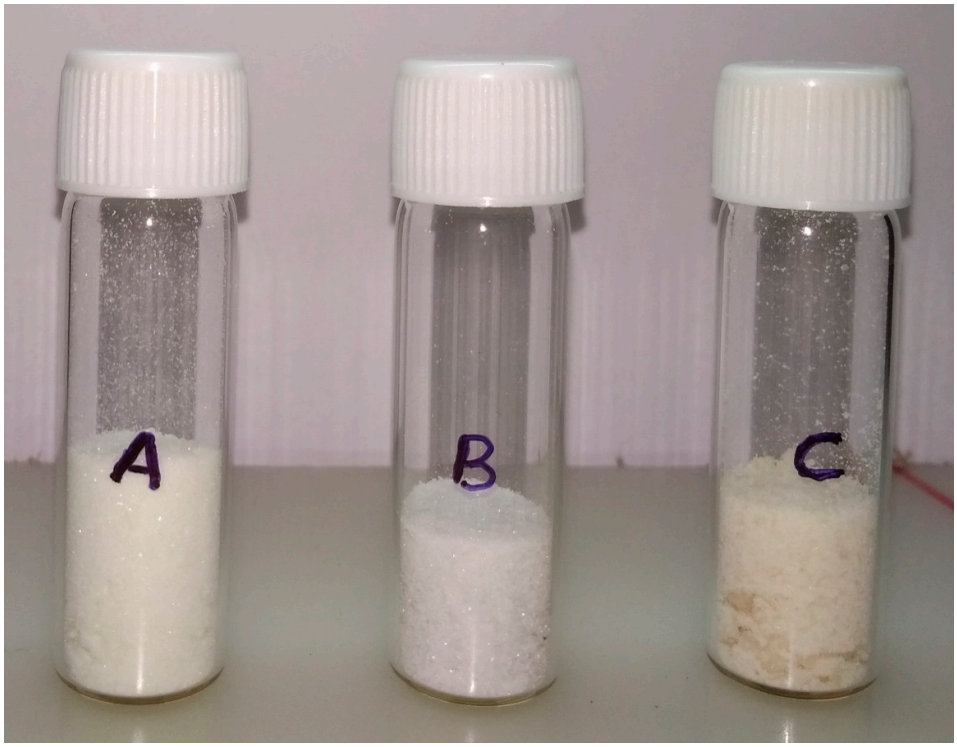


Figure 1. A gram-scale synthesis of (A) 4-nitrobenzylacetate, (B) 4-bromoacetanilide, and (C) 4-nitrophenylacetate under the optimized reaction conditions.

4. Materials and Methods

4.1. Materials

Alcohols, amines, phenols, and thiols were purchased from Sigma-Aldrich and used as received without further purification. Solvents were purchased from Merck and Sigma-Aldrich and used as received without any further purification processes.

4.2. General Procedure for the Acetylation of Alcohols, Phenols, Thiols, and Amines under Solvent-Free Conditions

In a typical reaction, a 25 mL round-bottom flask was charged with 1 mmol of substrate (amine, alcohol, phenol, or thiol) followed by the addition of 1.5 mmol acetic anhydride. This mixture was homogeneously mixed with the help of a glass rod and later placed in a preheated oil bath maintained at 60 °C for the required time. A known amount of sample was taken periodically from the reaction mixture at different time intervals and diluted with diethyl ether to monitor the completion of the reaction by gas chromatography. Furthermore, the conversion and selectivity were also determined by gas chromatography at a given time. After completion of the reaction, the mixture was diluted with diethyl ether and washed two times with sodium bicarbonate, and then the ether layer was dried with sodium sulfate. Conversion and selectivity were determined by Agilent gas chromatography using an internal standard method. The products were characterized by ^{1}H-NMR and GC-MS (Supporting Information; Figures S1–S23).

5. Conclusions

In summary, we have developed a convenient and general method for the acetylation of alcohols, amines, phenols, and thiols in the absence of solvent and catalyst. The experimental conditions were milder, and the reactions were completed in shorter reaction times. Interestingly,

most of the substrates were transformed to their respective acetylated products in higher yields under the optimized reaction conditions. The synthesized products were characterized by GC-MS and their purity were confirmed by ^{1}H-NMR spectra.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1. GC-MS spectra for all the acetylated compounds are given in the supporting information file.

Author Contributions: NA and MJ executed all the experiments while NN contributed to characterizing the products. AD planned the work and wrote the manuscript and JMVKK assisted in writing the manuscript.

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