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Original Article

Acetylation of alcohols and amines catalyzed by onion peel ash under a base- and solvent-free condition

Poh Wai Chia[1, 2*], Poh Seng Chee[1], Noor Wini Mazlan[1],
Fu Siong Julius Yong[2], Mohd Zul Helmi Rozaini[2], and Su-Yin Kan[3]

[1] *Faculty of Science and Marine Environment, Universiti Malaysia Terengganu,*
Kuala Terengganu, Terengganu, 21030 Malaysia

[2] *Institute of Marine Biotechnology, Universiti Malaysia Terengganu,*
Kuala Terengganu, Terengganu, 21030 Malaysia

[3] *Faculty of Health Sciences, Universiti Sultan Zainal Abidin,*
Kuala Nerus, Terengganu, 21300 Malaysia

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Abstract

This manuscript describes a facile and environmentally benign protocol for the acetylation of various alcohol and amines catalyzed by onion peel ash under a base- and solvent-free condition. Various acetates were successfully prepared from the alcohols and amines using onion peel ash as a catalyst and the end-products were obtained in good to excellent yields (76−96%). The current reported protocol complies with green chemistry principles, such as a base- and solvent-free condition, mildness of the reaction, and a recyclable catalytic system up to four times. Furthermore, the current method allows the management of the abundant onion peel bio-waste into a more useful catalyst in the field of organic synthesis. The transformations of bio-wastes into catalysts for organic reactions are of interest and highly sought after by scientists to meet the goal for a more sustainable chemistry in the near future.

Keywords: acetylation, alcohols, amines, onion peel ash, recyclable catalytic system

1. Introduction

In recent years, environmental pollution and socioeconomic impacts associated with the disposal of chemical wastes to the environment have accelerated the research and adoption of green chemistry (Mirjafari, 2014; Azizi & Dezfooli, 2016). In particular, the development of new and recyclable catalysts in the field of organic synthesis that are capable of facilitating copious numbers of products are of considerable interest because it minimizes the amount of waste introduced into the environment (Adenot, Landstrom, Gallou, & Lipshutz, 2017; Maleki, Ravaghi, Aghaei, & Movahed, 2017). To date, researchers are attracted to the use of catalytic systems which utilize water and water extracts of bio-wastes in achieving organic transformations (Chia, Poh, Mohd, Yong, & Kan, 2018; Bakherad, Keivanloo, Gholizade, Doosti, & Javanmardi, 2017). In addition, much literature has also reported on the advantages of using water extract of bio-wastes as solvents or catalytic systems in organic reactions, such as the Suzuki cross-coupling reaction (Sarmah, Dewan, Thakur, & Bora, 2017), Sonogashira reaction (Dewan, Sarmah, Bora, & Thakur, 2017), Michael addition (Kumar, Bheeram, Mukkamala, Rao, & Vasantha, 2018), Ullman coupling (Jangam, Appa, Bandameeda, Loka, & Katta, 2018), and synthesis of 2-amino-4H-chromenes (Kantharaju & Khatavi, 2018). From the perspective of green chemistry,

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*Corresponding author
Email address: pohwai@umt.edu.my

these catalytic systems possess many advantages including abundant bio-waste resources, inexpensive and high reaction yields, and recyclable catalytic systems, which render these catalytic systems as attractive tools in organic reactions.

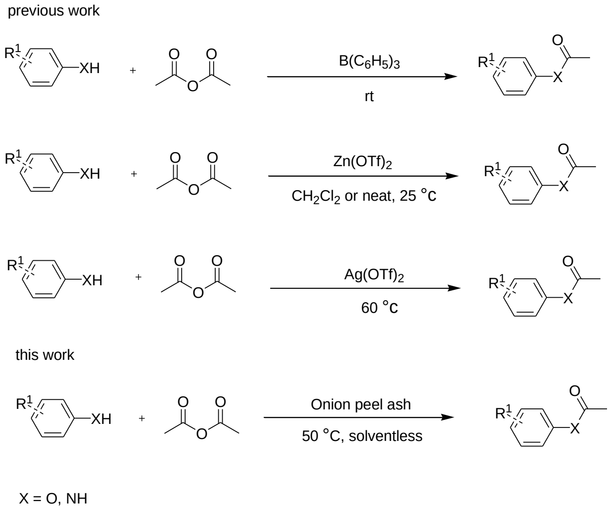
Functional group protection, such as the acetylation of alcohol and amino groups, are central towards the synthesis of targeted molecules. The protection of alcohol and amino groups via an esterification reaction for the synthesis of acetate are important organic transformations for the preparation of many important synthetic products such as perfumes, food additives and flavors, plasticizers, medicines, and polymers (Das & Chakraborty, 2011). Generally, base- and acid-mediated acetylation of alcohol and amino groups are the common methods to achieve the synthesis of acetate (Saravanan & Singh, 1999). Other methods for the preparation of acetates include the use of 4-dimethylaminopyridine (DMAP) (Scriven, 1983), magnesium powder (Bajracharya, & Shrestha, 2018), nanoparticle (Veisi, Taheri, & Hemmati, 2016), $Fe(OTs)_3 \cdot 6H_2O$ (Baldwin, Nord, O'Donnell, & Mohan, 2012), tribromo melamine (Hajjami, Ghorbani-Choghamarani, Karamshahi, & Norouzi, 2014), tris (pentafluorophenyl) borane (Prajapti, Nagarsenkar, & Babu, 2014), $Zn(OTf)_2$ (Kumar, Reddy, Reddy, & Bandichhor, 2014), and manganese (Joo, Youn, Hwang, & Kim, 2017). Unfortunately, most of these catalytic systems suffer from several drawbacks, such as the use of external metals, expensive reagents, non-recyclable catalytic systems, and reagents which are toxic to human health and the environment. As such, researchers are inspired to develop a simple yet green catalytic system for this important organic transformation in the organic synthesis of many promising compounds.

In this regard, this work is devoted to the synthesis of acetates via the esterification of alcohol and amines using acetic anhydride in the presence of onion peel ash under an acid-, base-, and solvent-free condition (Scheme 1). Every year, about 100,000 tons of onion waste products are generated. If this bio-waste is sent directly to landfill without proper treatment, it can lead to adverse consequences to our environment, (Gao, Li, Geng, Wei, & Zhang, 2015; Sharma, Mahato, Nile, Lee, & Lee, 2016). Onion peel ash can be used as a green catalyst that is capable of overcoming environmental pressure exerted by onion peel waste products, and at the same time, provides an alternative to managing this bio-waste material (Chia, Lim, Yong, Poh, & Kan, 2018; Chia *et al.*, 2019). Furthermore, the current work encompasses the use of a more sustainable methodology to prepare the acetates, which holds promising potential to overcome the drawbacks of conventional methods faced by scientists.

2. Experimental

2.1 Materials and methods

All reagents and solvents were purchased from Sigma-Aldrich Malaysia and used without further purification. The ^1H and ^{13}C-NMR characterizations were performed using Bruker Avance III 400 spectrometer with $CDCl_3$ as the solvent. The GC-MS analysis was performed using Shimadzu QP2010SE installed with a Supelco fused silica capillary column (30 m × 0.25 mm i.d., 0.25 mm film thickness).



Scheme 1. Synthetic routes toward the preparation of acetates.

2.2 Procedure for the preparation of onion peel ash

Onion waste samples were collected from a nearby local waste disposal site at Kuala Terengganu, Malaysia on March 2018. The onion peels were separated from the bulb and washed with distilled water (30 mL × 3). The onion peels were left 2 days for air-drying and sliced into small pieces. About 2.0 g of onion peel were then burnt in the furnace at 500 ºC for about 1 h. The obtained ash was termed as onion peel ash and used as a catalyst in the preparation of acetates.

2.3 Typical synthesis procedure for acetylation reaction

A mixture of alcohol or amino (1.00 mmol), acetic anhydride (1.1 mmol) and onion peel ash (20 mg) was heated at 50 ºC for 1 h. The reaction mixture was quenched with water (5 mL) and added to ethyl acetate (3 × 10 mL). The organic layer was separated, washed with sodium bicarbonate, and dried using $MgSO_4$ before concentration under reduced pressure. The crude product was subjected to silica gel column chromatography purification with ethyl acetate/hexane (1:9) as its eluent. All end-products were characterized using NMR spectroscopy (^1H and ^{13}C), which were then further supported by gas chromatography-mass spectrometry (GC-MS) analysis.

2.4 Spectroscopic data of selected compounds

Phenyl acetate **3a** ^1H-NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (t, J = 7.39 Hz, 2H); 7.18-7.14 (t, J = 7.43 Hz, 1H); 7.05-7.03 (d, J = 8.54 Hz, 2H); 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.48, 150.78, 129.47, 125.75, 121.57, 21.09 ppm; GC-MS: $C_8H_8O_2$, m/z 136.05.

4-Nitrophenyl acetate **3b** ^1H-NMR (400 MHz, $CDCl_3$): δ 8.17-8.15 (d, J = 9.1 Hz, 2H); 7.20-7.18 (d, J = 9.1 Hz, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.31, 155.41, 155.28, 125.17, 20.79 ppm; GC-MS: $C_8H_7NO_4$, m/z 181.04.

4-Bromophenyl acetate **3c** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.47-7.44 (d, *J* = 8.81 Hz, 2H); 6.96-6.94 (d, *J* = 8.81 Hz, 2H); 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.06, 149.68, 132.39, 123.43, 118.79, 21.14 ppm; GC-MS: $C_8H_7BrO_2$, m/z 213.96.

N-Phenylacetylamide **3g** ^{1}H-NMR (400 MHz, CD Cl$_3$): δ 7.87 (brs, 1H); 7.51 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 2H), 2.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.91, 138.00, 128.86, 124.24, 120.12, 24.37 ppm; GC-MS: C_8H_9 NO, m/z 135.07.

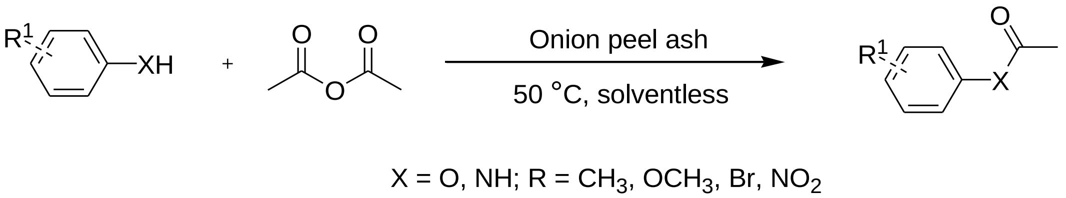
N-(4-Methylphenylacetyl)amide **3e** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.3 Hz, 2H); 7.27 (brs, 1H); 7.10 (d, *J* = 8.3 Hz, 2H); 2.30 (s, 3H); 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.03, 135.59, 133.52, 129.38, 120.35, 24.37, 20.94 ppm; GC-MS: $C_9H_{11}NO$, m/z 149.08.

N-(3-Methoxyphenylacetyl)amide **3k** ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.61 (brs, 1H); 7.26-7.14 (m, 2H); 6.97 (d, *J* = 7.9 Hz, 1H); 6.64 (d, *J* = 7.9 Hz, 1H); 3.77 (s, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.36, 160.00, 139.39, 129.60, 112.53, 109.89, 106.05, 55.22, 24.43 ppm; GC-MS: $C_9H_{11}NO_2$, m/z 165.08.

3. Results and Discussion

Phenol was chosen as the model substrate to determine the optimized reaction condition. Initially, phenol (0.01 mmol) was added into a 25 mL round bottom flask containing acetic anhydride (0.01 mmol) and onion peel ash (5 mg). The reaction mixture was heated to 50 °C. After heating the reaction mixture for 1 h, only a 50% yield of **3a** was obtained (Table 1, entry 2). The preliminary results indicated that the onion peel ash played a crucial role in facilitating the formation of phenyl acetate (**3a)**. In addition, we found that **3a** was obtained in excellent yield when 20 mg of onion peel ash was used (Table 1, entries 5). However, when the synthesis of **3a** was repeated under identical reaction conditions without the onion peel ash, only a trace amount of **3a** was detected (Table 1, entry 1). The reaction condition might also be affected by the temperature. In this case, we also studied the temperature used for the synthesis of **3a.** The yield of **3a** was the highest yield when 50 °C was used and a rise in temperature did not lead to a better yield of **3a** (Table 1, entries 6–9). Next, the reaction time for the synthesis of **3a** was also evaluated and 60 min was found to be the optimum time in the preliminary reaction (Table 1, entries 10–16). A controlled experiment was also set up to study the effect of different solvents used for the synthesis of **3a**. In this regard, various solvents were chosen to synthesize **3a** (dimethylformamide (DMF), dimethylsulfoxide (DMSO), CH_3CN, CH_3OH, CH_3CH_2OH) under the identical reaction conditions and the yields of **3a** were found to decrease (93% for DMF, 89% for DMSO, 83% for CH_3CN, 90% for CH_3OH, and 91% for CH_3CH_2OH) (Table 1, entries 17−21). The optimum yield of **3a** was obtained (96% yield) when the neat condition was applied (Table 1, entry 8). Thus, the optimum reaction condition was determined to be: 60 min, 50 °C, and 20 mg of onion peel ash in a solvent-less condition (Table 1, entry 8).

Table 1. Optimization of reaction condition for **3a**.

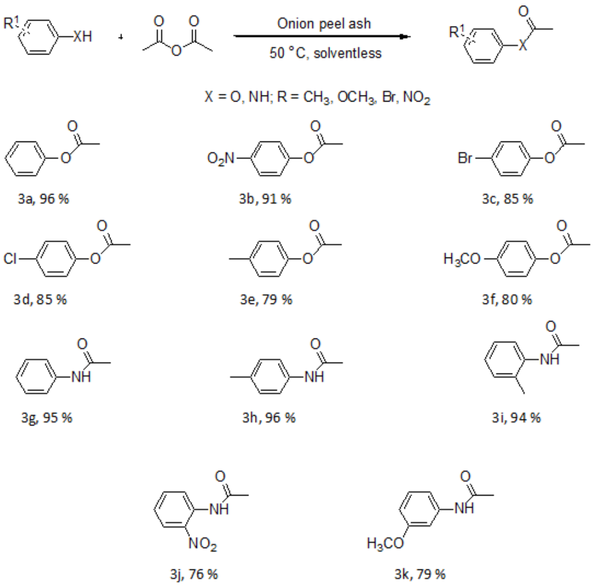


Entry	Solvent (mL)	Catalyst (mg)	Time (min)	Temperature (°C)	Yield^a (%)
1	Neat	0	60	50	Trace
2	Neat	5	60	50	50
3	Neat	10	60	50	74
4	Neat	15	60	50	88
5	Neat	20	60	50	96
6	Neat	20	60	30	80
7	Neat	20	60	40	87
8	Neat	20	60	50	96
9	Neat	20	60	60	95
10	Neat	20	20	50	85
11	Neat	20	30	50	87
12	Neat	20	40	50	90
13	Neat	20	50	50	92
14	Neat	20	60	50	96
15	Neat	20	90	50	95
16	Neat	20	120	50	94
17	Neat	20	60	50	93
18	Neat	20	60	50	89
19	Neat	20	60	50	83
20	Neat	20	60	50	90
21	Neat	20	60	50	91

^{a}Isolated yield of product **3a**.

Next, we investigated the general applicability of the current catalytic system through the synthesis of acetates using different alcohols. In the case of acetylation of alcohols, the acetates were prepared in good to excellent yields and it worked well with all of the substituent groups (MeO, Me, NO_2, Br, and Cl) (Scheme 2). We also extended the scope of the study to synthesize amides by reacting different amines with acetic anhydride (**3g**-**k**). In all cases, the amides were prepared in good to excellent yields, judging by the isolated yields (76−96%). The rate of reaction for the electron-deficient group (**3j**) was found to decrease and this was possibly due to the destabilizing effect caused by this functional group, which made the amino to be less nucleophilic and thus recorded a lower yield compared to the others. The current catalytic system was found to be efficient and unprecedented as no external bases or catalysts were required in the preparation of acetates and amides. The prepared products of **3a-k** were characterized using NMR (^1H and ^{13}C) and further supported by GC-MS analysis.

Furthermore, we examined the recyclability of the current catalytic system by using the synthesis of **3a** as a model reaction (Table 2). Upon completion of the first cycle, the onion peel ash was recovered and washed with distilled water and was subjected to the subsequent synthesis of **3a**. The results indicated that the onion peel ash catalyst could be recovered and reused up to four times without significant loss in efficiency judging by the isolated yields of **3a**. This result may also imply that the current catalytic system is aligned to the goal of green chemistry.

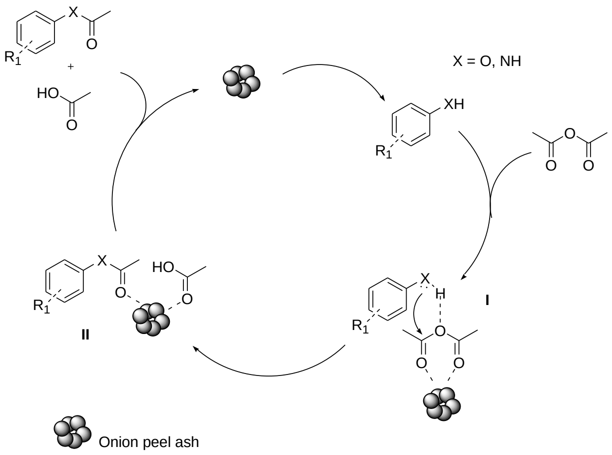


Scheme 2. Onion peel ash facilitation of acetylation of alcohols and amines.

Table 2. Recyclability study of onion peel ash catalyst for synthesis of **3a**.

Cycle	Yield (%)[a]
Initial run	96
1st run	95
2nd run	93
3rd run	93
4th run	90

[a] Isolated yields. Reaction conditions: Phenol (1 mmol), Acetic anhydride (1 mmol), Onion peel ash (20 mg), solventless, 50 °C, in air.



Scheme 3. Proposed mechanism for the synthesis of acetates and amides.

Based on our understanding on the mechanism of acetylation on alcohols and amines (Qayum, Kumar, Basha, & Srinivas, 2014), a plausible mechanism is proposed (Scheme 3). At first, the oxygens on the acetic anhydride form weak interactions with the onion peel ash catalyst and weak hydrogen bonding was formed between the alcohols or amines as shown in the intermediate **I** in a base- and solvent-free condition. Next, we envisioned that the alcohols or amines donated their protons and were bound to either side of acetic anhydride, which led to the formation of intermediate **II**. Finally, the products, namely the acetates or amides and acetic acids, were separated from the onion peel catalyst and this catalyst was released and the catalytic cycle was repeated. In our work, the metal content of onion peel ash (2.0 g) was analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The results of ICP-OES were Ca (52177.00±5.22 ppm), K (22927.00±0.47 ppm), Na (14930.00 ±0.21 ppm), Mg (7896.00±6.26 ppm), S (2225.00±1.44 ppm), P (2172.00±2.13 ppm), Fe (1815.00±1.03 ppm), Al (1366.00± 1.07 ppm), Sr (300.00±2.52 ppm), Mn (216.00±2.18 ppm), B (107.00±0.09 ppm), Ba (53.00±0.23 ppm), Zn (52.00±0.11 ppm), Rb (35.00±0.02 ppm), La (15.00±0.31 ppm), Ga (15.00±0.12 ppm), Cu (13.00±0.17 ppm), and Pb (9.80±0.23 ppm). Based on the ICP-OES results and previous studies (Sarvari, & Sharghi, 2005; Vishvanath, Nagesh, Ketan, & Prathamesh, 2015; Yadav, Lagarkha, & Balla, 2010), the metals in the onion peel ash may act as Lewis acids that facilitate the formation of various acetates and amides as demonstrated in this work. In addition, we have repeated the synthesis of 3a using a catalytic amount of zinc chloride under a solvent-free condition and the yield of **3a** was found to be satisfactory (91%). On a final note, the current catalytic system offers many interesting features that are eco-friendliness, recyclable catalytic system, high reaction yield, and bio-waste recycling, which encourage a more sustainable way of synthesis and management of the current bio-waste. Table 3 shows the merits of the current work compared to

Table 3. Synthesis of **3a** catalyzed by different methods.

Entry	Catalyst	Yield (%)	Reference
1	Onion peel ash	96	Current work
2	Magnesium powder	96	(Bajracharya, & Shrestha, 2018)
3	Polydopamine sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles	96	(Veisi, Taheri, & Hemmati, 2016)
4	Tris(pentafluorophenyl) borane	92	(Prajapti, Nagarsenkar, & Babu, 2014)
5	Zinc triflate	98	(Kumar, Reddy, Reddy, & Bandichhor, 2014)
6	Zinc chloride	40	(Yadav, Lagarkha, & Balla, 2010)
7	Magnesium chloride	95	(Vishvanath, Nagesh, Ketan, & Prathamesh, 2015)
8	Manganese Iodide	80	(Joo, Youn, Hwang, & Kim, 2017)
9	Ferric triflate	98	(Qayum, Kumar, Basha, & Srinivas, 2014)
10	Tetrakis(acetonitrile)copper(I) triflate	98	(Mensah, & Earl, 2017)
11	Silver triflate	92	(Das & Chakraborty, 2011)

previous methods and their yields in the synthesis of **3a**. In most cases, the acetylation of alcohols and amines were achieved using environmentally hazardous and non-recyclable catalysts. In this work, we demonstrated that onion peel can be recyclable and converted into a useful catalyst, which are of interest and highly sought after by scientists to meet the goal for a more sustainable chemistry in the near future (Tan, Chuah, & Chia, 2016).

4. Conclusions

In summary, a green and recyclable onion peel ash catalytic system was developed to synthesize various acetates and amides by reacting different alcohols and amines in a solvent- and base-free condition. Under the improved protocol, the yields of the end-products were obtained in good to excellent yields (76−96%) and the current catalytic system could be reused up to four times without significant loss of efficiency. We also tried to understand the underlying mechanism that contributed to the formation of various acetates and amides by proposing a plausible mechanism. We envisioned that the current catalytic system will be of great utility in other organic transformations in the field of green synthesis.

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