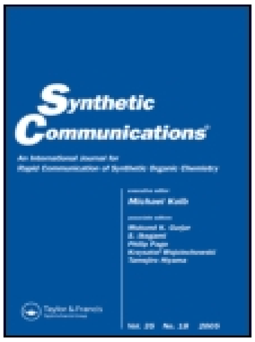

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SOLID-PHASE BENZOYLATION OF PHENOLS AND ALCOHOLS IN MICROWAVE REACTOR: AN ECOFRIENDLY PROTOCOL

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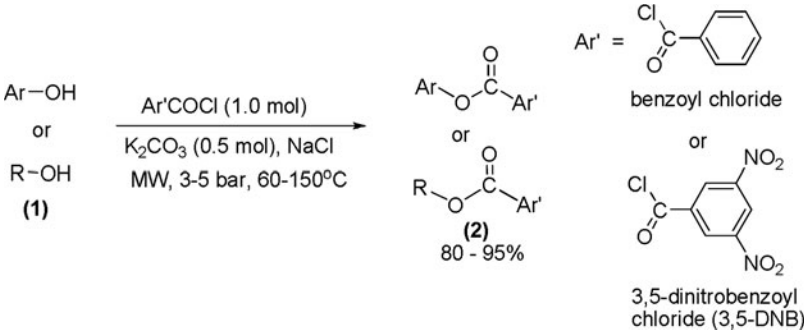
GRAPHICAL ABSTRACT



Abstract *An efficient solid-phase benzoylation of phenols and alcohols was developed under microwave irradiation. A stoichiometric amount of benzoyl chloride was sufficient to carry out the reaction. This benzoylation features short reaction time, good yields, and easy workup procedures. Furthermore, the scope of the reaction was extended to prepare 3,5-dinitrobenzoyl derivatives of alcohols.*

Keywords Benzoyl chloride; benzoylation; 3,5-dinitrobenzoyl chloride; ecofriendly method; microwave reactor; solid-phase reaction

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INTRODUCTION

The formation of esters is one of the most extensively used techniques for the protection of hydroxyl group of alcohols and phenols in organic chemistry.[1] The protection of hydroxyl groups is often vital in the course of various transformations in a synthetic sequence, particularly in the preparation of polyfunctional natural products such as nucleosides, steroids and carbohydrates, and even in synthetic products such as perfumes, cosmetics, flavors and food additives, pharmaceuticals, plasticizers, and polymers.[2] Benzoylation of the hydroxyl group of corresponding phenols and alcohols is one of the most useful protection protocols for this purpose. In addition, benzoylation of phenols and alcohols have significant academic concerns as it is used for the characterization and identification of such compounds.[3] A critical literature survey[4–17] indicates that there are large numbers of methodologies on acetylation to block the hydroxyl group of phenols and alcohols. However, derivatization of phenols and alcohols through benzoylation are equally demanding. In a search of benzoylation for phenols and alcohols, very few protocols have been reported. There was a method where benzoylation of simple phenol was executed by using benzoyl chloride in the presence of potassium carbonate in benzene solution.[18] However, benzoylation of phenols and alcohols is generally carried out with benzoyl chloride[19,20] under different catalytic conditions using various catalysts[21] such as ZnO, TiO_2, CuO, trifluoromethanesulphonic acid, and zinc dust. There was another study on the benzoylation of substituted phenols under phase-transfer catalytic conditions.[22] Further, benzoylation of phenols and alcohols were accomplished by 3,5-dinitrobenzoyl chloride[23] and benzoic anhydride under different catalytic conditions such as cobalt nitrate,[24] zirconyl triflate, $ZrO(OTf)_2$,[25] and hydrotalcite.[26] All these methods were found to be executed under expensive catalytic conditions or through the use of exotic reagents. Some of these methods are associated with longer reaction time and poor yields. In the well-known Schotten–Baumann method[19,20] used for the preparation of the derivatives of phenols, benzoyl chloride is used in excess under alkaline conditions, and the benzoyl derivative frequently occludes unreacted benzoyl chloride, which is excluded from hydrolysis and causes critical problem in separating the product. Thus an environmentally safe, cost-effective, high-yielding method is required for the benzoylation of phenols and alcohols.

Now exploitation of cleaner technology has a major emphasize in green chemistry. Use of large excess of solvents required as a medium for chemical reaction also induces ecological and economic concerns.[27] Nowadays, microwave (MW)–assisted chemistry is one of the most accepted innovative techniques. The microwave-activated organic reactions are associated with decreasing reaction time, increased product yield, cleaner reaction with easier workup, and reduced effluent load.[28] The MW dielectric heating effect induces polar liquids and solids to transform the electromagnetic energy into heat to accelerate the chemical reactions.[29] Thus, a few microwave-based methodologies were developed for the benzoylation using Bu_2SnO[30] and montmorillonite[31] acidic clays. Consequently, considering the importance of benzoylation and environmental factors, as well as our interest in green chemical processes without any costly catalyst, herein we contemplated a generalized and utilitarian microwave-assisted, facile, ecofriendly, high-yielding, solvent-free benzoylation of phenols with stoichiometric amount of benzoyl chloride and alcohols with 3,5-dinitrobenzoyl chloride (3,5-DNB) respectively in the presence of K_2CO_3 using a microwave reactor.

RESULTS AND DISCUSSION

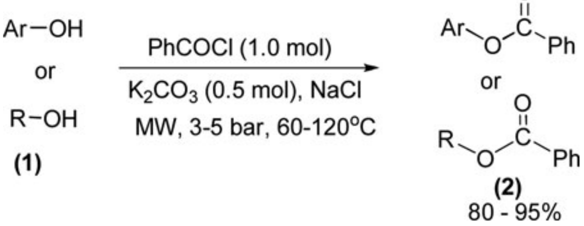
To execute this concept, a mixture of phenolic compound or alcohol and potassium carbonate was treated with a stoichiometric amount of benzoyl chloride and the reaction mixture was irradiated under microwave at controlled temperature and pressure in solvent-free conditions to furnish the benzoylation product (Scheme 1).

The effective development of brine-mediated benzoylation[32] as well as acetylation[33] of amines in our laboratory motivated us to carry out this benzoylation in the presence of sodium chloride in the solid phase. The presence of solid sodium chloride made the solid mass porous, for which the isolation of the benzoates became easier, and this also led to better yield as tabulated in Table 1.

Now the required benzoylation was initially carried out with a 1:1 molar ratio of phenol and base, such as K_2CO_3. However, it led to the formation of low yield, as most probably benzoyl chloride was depleted in the presence of excess base. Then reducing the load of excess base, equivalent amount of substrates and base were taken without and with sodium chloride. In each case the maximum conversion was recorded for 2 min as depicted in Fig. 1.

To demonstrate the advantage of this protocol, at first benzoylation of phenols or alcohols was attempted under conventional thermal condition in an open vessel as well as in sealed vessel (silicon carbide vessel with Teflon cap, Anton Paar) at the corresponding condition with that of microwave (MW). In the case of open system phenols were mostly oxidized under reaction conditions which led to very poor yield. However, benzoylation under sealed condition in an oil bath at comparable temperature as that of MW required longer reaction time with poor yield, as specified in Table 2. Often, during thermal heating a portion of the reaction mixture was carbonized and the Teflon cap of the sealed vessel released toxic vapor of benzoyl chloride due to excess pressure produced inside the vessel.

Thus, to extend the scope of the reaction, it was investigated over different phenols and alcohols as depicted in Table 3. Phenols or alcohols were mixed thoroughly with anhydrous potassium carbonate and solid sodium chloride in a mortar and the reaction mixture was transferred into the quartz microwave vessel (in the case of liquid substrates, it was added directly to the anhydrous potassium carbonate and sodium chloride mixture in the vessel). Then a neat stoichiometric amount of benzoyl



Scheme 1. Solid-phase benzoylation of phenols and alcohols in microwave reactor.

Table 1. Standardization of reaction conditions using phenol (1.0 mole) as substrate

Run	Anhy. K_2CO_3 (mol)	NaCl (g)	Reaction time (% yield) 1 min	2 min	3 min
1	1.0	—	25	46	40
2	0.5	—	50	76	65
3	0.5	1.5	64	90	74

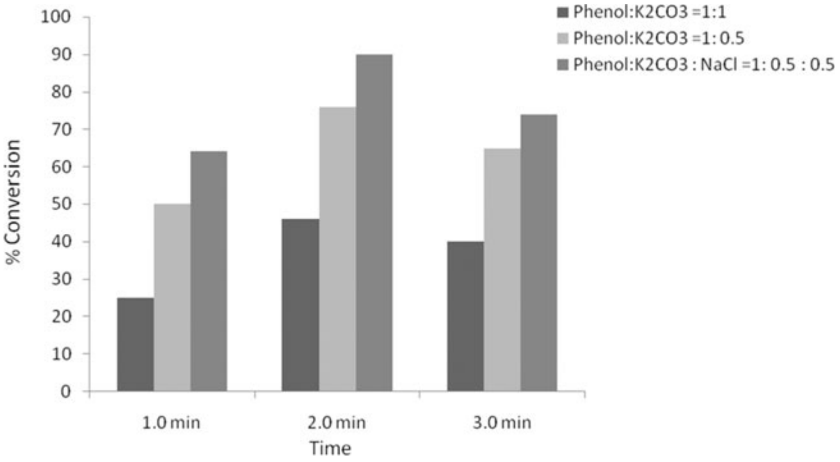


Figure 1. Effect of percentage of conversion with time under microwave irradiation.

Table 2. Comparison of benzoylation of alcohols/phenols under heating condition with MW

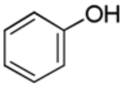
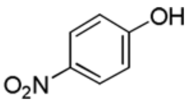
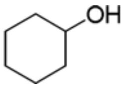
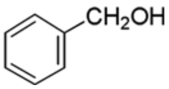
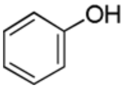
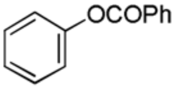
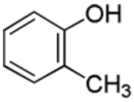
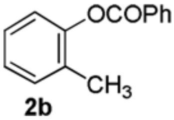
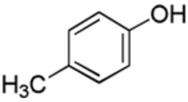
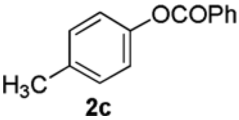
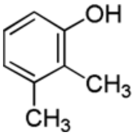
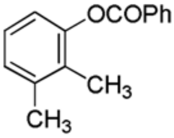
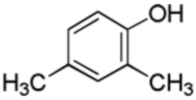
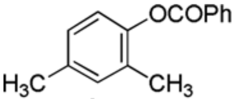
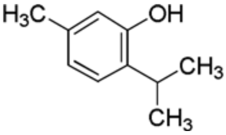
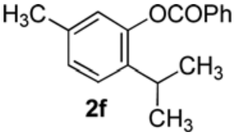
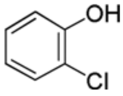
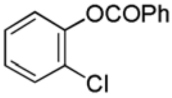
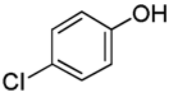
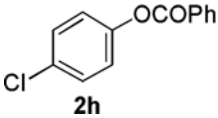
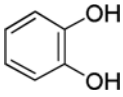
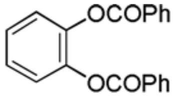
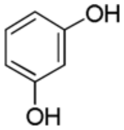
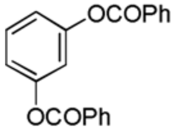
Substrate	Conventional heating temp./time (°C/min)	Yield (%)	Microwave heating pressure/temp./time (bar/°C/min)	Yield (%)
	60–70/15	30	4.8/64/2	90
	130–150/20	48	3.4/140/3	82
	70–90/15	36	3.5/80/2	85
	70–90/10	24	3.6/80/2	82

Table 3. Benzoylation of phenols and alcohols

Entry	Reactant	Product[a]	Reaction conditions pressure/temp./time (bar/°C/min)	Yield (%)[b]
1		 **2a**	4.8/64/2	90
2		 **2b**	3.6/140/2	93
3		 **2c**	3.2/75/2	92
4[d]		 **2d**	3.7/ 60/2	93[c]
5		 **2e**	3.5/60/2	80
6		 **2f**	4.0/50/2	83[c]
7		 **2g**	3.4/65/2	84
8		 **2h**	3.2/95/2	86[c]
9		 **2i**	3.5/90/2	70
10		 **2j**	3.6/120/2	72

(Continued)

Table 3. Continued

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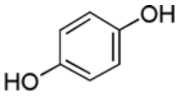
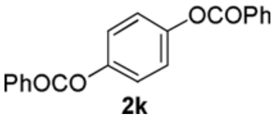
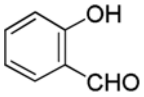
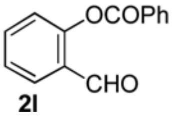
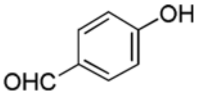
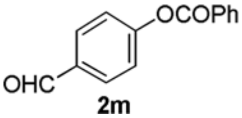
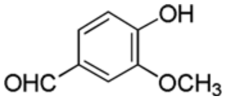
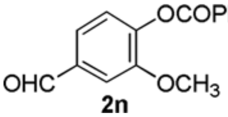
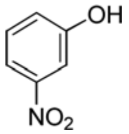
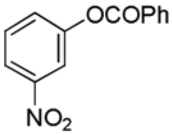
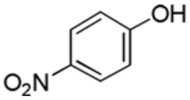
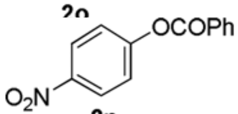
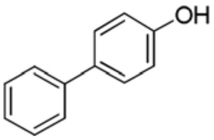
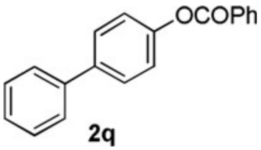
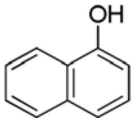
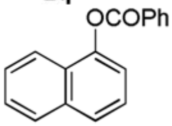
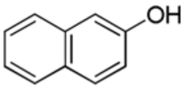
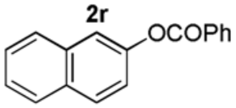
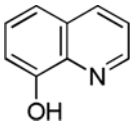
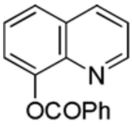
11		 **2k**	3.8/150/2	68[c]
12		 **2l**	2.5/70/2	85[c]
13		 **2m**	2.4/80/2	87
14		 **2n**	2.8/75/2	91[c]
15		 **2o**	3.6/80/2	76
16		 **2p**	3.4/140/3	82[c]
17		 **2q**	4.2/150/3	90
18		 **2r**	2.6/70/2	78
19		 **2s**	3.6/100/2	86[c]
20		 **2t**	3.2/110/2	88[c]

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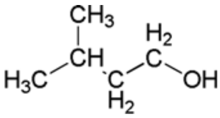
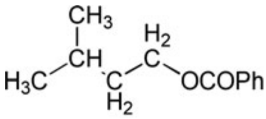
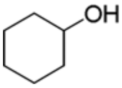
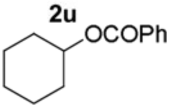
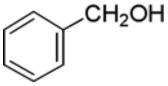
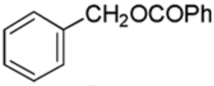
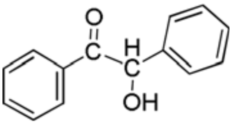
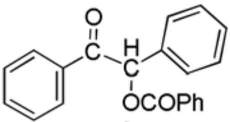
Table 3. Continued

Entry	Reactant	Product[a]	Reaction conditions pressure/temp./time (bar/°C/min)	Yield (%)[b]
21		 **2u**	3.8/60/2	78
22		 **2v**	3.5/80/2	85
23		 **2w**	3.6/80/2	82
24		 **2x**	4.8/135/4	92[c]

[a] All products were characterized by ^{1}H and ^{13}C NMR and IR, and their data are identical with the reported value in the literature.

[b] The yield refers to isolated yield.

[c] ^{1}H and ^{13}C NMR, IR, and HRMS are data reported for the compound.

[d] Unknown compound.

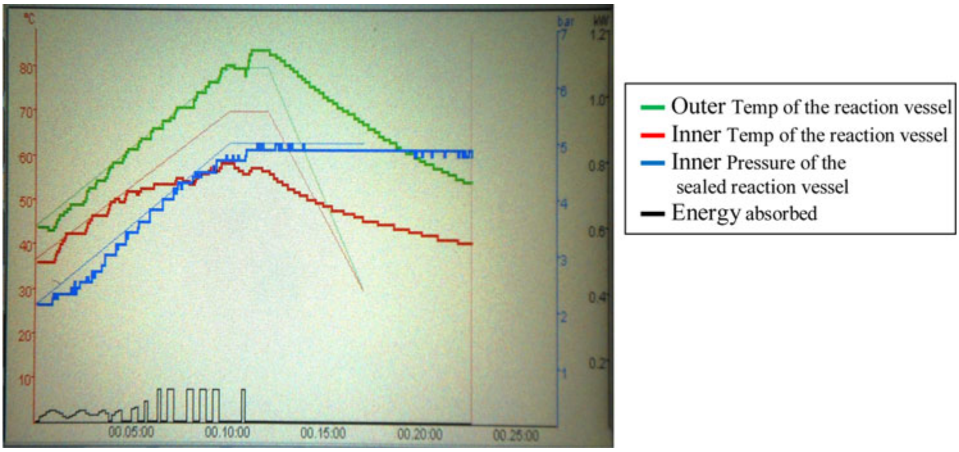
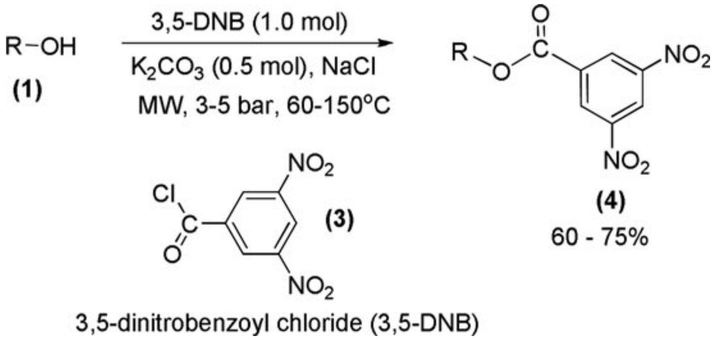
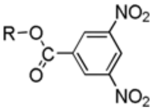
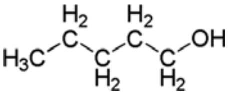
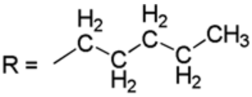
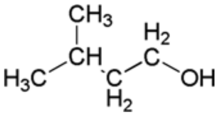
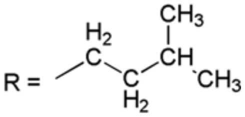
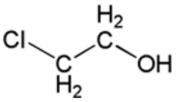
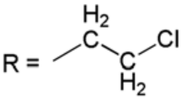
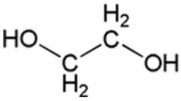
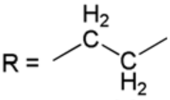
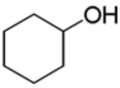
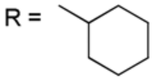
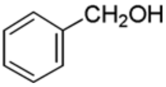
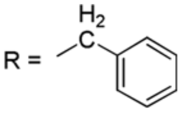


Figure 2. Graph for the progress of the reaction in microwave reactor.



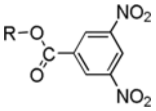
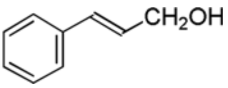
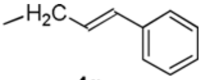
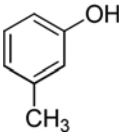
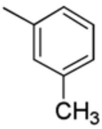
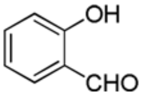
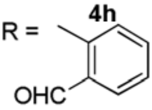
Scheme 2. Solid-phase benzoylation using 3,5-dinitrobenzoyl chloride in microwave reactor to obtain solid derivative.

Table 4. 3,5-DNB derivatives of alcohols/phenols

Entry	Alcohols/phenols	3,5-Dinitrobenzoates[a] 	Reaction conditions pressure/temp./time (bar/°C/min)	Yield (%)[b]
1		 **4a**	3.9/70/2	90
2[d]		 **4b**	4.2/70/2	93[c]
3		 **4c**	3.5/90/2	76[c]
4		 **4d**	4.6/120/2	84
5		 **4e**	4.6/110/2	92[c]
6		 **4f**	4.3/120/2	88[c]

(Continued)

Table 4. Continued

Entry	Alcohols/phenols	3,5-Dinitrobenzoates[a] 	Reaction conditions pressure/temp./time (bar/°C/min)	Yield (%)[b]
7[d]		R =  **4g**	4.1/120/2	74[c]
8		R =  **4h**	5.3/150/2	86
9[d]		R =  **4i**	4.5/120/2	72[c]

[a] All products were characterized by ^{1}H and ^{13}C NMR and IR, and their data are identical with the reported values in the literature.

[b] The yield refers to isolated yield.

[c] ^{1}H and ^{13}C NMR, IR, and HRMS are data reported for the compound.

[d] Unknown compound.

chloride was added to the reaction vessel and this was subjected to microwave irradiation under sealed conditions (100 W, 2–5 bar, 60–150 °C) for 2–3 min.

After the completion of the reaction, the benzoates were isolated via usual workup as necessary. All the derivatives were recrystallized from methanol or methanol/water and identified by comparison with authentic samples and their NMR spectra. The reaction conditions were monitored on the microwave reactor screen and thus the progress of the reaction was obtained as in Fig. 2.

To get insight into the reaction, it is expected that greater concentrations of chloride ions through the presence of sodium chloride in the reaction mixture slowed down the decomposition of benzoyl chloride and thus enhanced its efficiency. Again in the presence of sodium chloride, the reaction mass became porous and so it was easier to isolate the product from water. The role of potassium carbonate was to remove the liberated hydrogen chloride from the reaction medium. After the completion of the reaction, the reaction mixture was poured into water, and the aqueous medium was found to be weakly alkaline.

Now, particularly in the case of alcohols the benzoates are usually liquid or low-melting solid. However, derivatization needs the isolation of a sharp-melting solid. This channelized us further to investigate the possible extension of this methodology to prepare the solid benzoyl derivatives of alcohols and some phenols.

Thus solid 3,5-dinitrobenzoyl chloride was taken in the place of benzoyl chloride in a somewhat modified form (Scheme 2).

In this case, solid 3,5-dinitrobenzoyl chloride, anhydrous potassium carbonate, and sodium chloride were mixed thoroughly and the substrate was poured into it. The reaction mixture was subjected to microwave irradiation (100 W, 3–4 bar, 80–90 °C) for 1 min. The usual work up led to the formation of solid 3,5-dinitrobenzoyl derivative (Table 4).

CONCLUSION

In summary, an efficient, inexpensive, high-yielding, and ecofriendly benzoylation of phenols as well as alcohols using benzoyl chloride and 3.5-dinitrobenzolyl chloride are developed under solvent-free conditions. Further, this protocol utilizes inexpensive common reagents without any costly catalysts that are normally used for the other MW solid-phase reactions. At the same time, faster rate of this microwave reaction, milder reaction conditions, and easy workup all make it superior.

EXPERIMENTAL

Melting points were determined in open capillaries using a Zeal 76-mm immersion thermometer. Reagent-grade chemicals were purchased from a commercial source and used without further purification. Microwave reactions were carried out by using Milestone microwave reactor Start*SYNTH*. Chemglass heavy-wall cylindrical pressure vessels (20 mL) with a Teflon bushing as a pressure seal were used for the sealed tube studies. IR spectra were recorded in KBr discs on Shimadzu FTIR-8300 and NMR spectra were recorded on a Bruker AV 500 instrument.

Typical Procedure for Benzoylation of Phenol

Phenol (2.0 mL, 20.0 mmol) was mixed with well ground K_2CO_3 (1.5 g, 10.0 mmol) and NaCl (1.5 g) mixture and transferred into the quartz reaction vessel. To this reaction mixture, benzoyl chloride (2.3 mL, 20.0 mmol) was added and mixed thoroughly. The reaction vessel was placed into the microwave reactor under sealed conditions with a stirrer and irradiated at the power of 100 W, 70 °C, and 5 bar (maximum pressure) for 2 min. During the reaction, the pressure of the reaction vessel raised to 4.8 bar. The completion of the reaction was monitored through TLC. After completion of the reaction, the reactor was allowed to cool along with the reaction vessel for 10 min. The reaction mixture was then poured into ice water. The solid product thus obtained was filtered and washed with cold water. It was then recrystallized from methanol/water to obtain the desired phenyl benzoate (**2a**), 3.5 g, 90% yield, mp 70 °C.[3]

Typical Procedure for 3,5-Dinitrobenzoyl Derivative of Cyclohexanol

3,5-Dinitrobenzoyl chloride (2.3 g, 10.0 mmol) was blended well with anhydrous K_2CO_3 (0.75 g, 5.0 mmol) and NaCl (0.75 g) in a mortar pestle. Then reaction mixture was taken in the microwave vessel, and cyclohexanol (1.0 mL, 10.0 mmol) was added to it and mixed thoroughly. The reaction vessel was positioned into the microwave reactor under sealed condition with a stirrer and irradiated at a power of 100 W, 110 °C, and 5 bar (maximum pressure) for 2 min. During the reaction, the reactor read the maximum pressure as 3.2 bar. After completion, the reactor was allowed to run for 10 min to purge the compressed air to cool the reaction vessel. The reaction mixture was then transferred into ice water. The solid product was then collected through filtration and washed with cold water. Then 3,5-dinitrobenzoate was purified by crystallization from methanol/water to furnish the product **4e**[34] in 2.7 g and 92% yield. The compound was recrystallised from MeOH to obtain white crystals, mp 113 °C. UV λ_{max}: 238 nm. IR (KBr, ν_{max} cm^{-1}): 3419, 2950, 1720, 1674, 1598, 1546 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.33–1.40 (m, 1H), 1.44–1.52 (m, 2H), 1.61–1.68 (m, 3H), 1.81–1.86 (m, 2H), 2.00–2.04 (m, 2H), 5.09–5.14 (m, 1H), 9.14 (d, *J* 7 Hz, 2H), 9.19 (s, 1H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 23.8 (×2), 25.2, 31.6 (×2), 75.9, 122.2, 129.4 (×2), 134.7, 148.7 (×2), 161.9. HRMS: m/z calcd. for $C_{13}H_{14}N_2O_6$: 317.0743 (M + Na); found 317.0745.

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SUPPLEMENTAL MATERIAL

Full experimental details, ^{1}H and ^{13}C NMR spectra, and additional references for this article can be accessed on the publisher's website.

REFERENCES

1. Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley: New York, 1999.
2. Baltork, I. M.; Aliyan, H.; Khosropour, A. R. Bismuth(III) salts as convenient and efficient catalysts for the selective acetylation and benzoylation of alcohols and phenols. *Tetrahedron* **2001**, *57*, 5851.
3. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry, 5th ed.*; Pearson Education: London, 2006.
4. Harton, D. 2-Acetamido-3,4,6-tri-*o*-acetyl-2-deoxy-α-D-glucopyranosyl chloride. *Org. Synth. Coll.* **1975**, *5*, 1.

5. Scriven, E. F. V. 4-Dialkylaminopyridines: Super acylation and alkylation catalysts. *Chem. Soc. Rev*. **1983**, *12*, 129.
6. Sano, T.; Ohashi, K.; Oriyama, T. Remarkably fast acylation of alcohols with benzoyl chloride promoted by TMEDA. *Synthesis* **1999**, 1141.
7. Vedejs, E.; Bennett, N. S.; Conn, L. M.; Diver, S. T.; Gingras, M.; Lin, S.; Oliver, P. A.; Peterson, M. J. Tributylphosphine-catalyzed acylations of alcohols: Scope and related reactions. *J. Org. Chem*. **1993**, *58*, 7286.
8. Borah, R.; Deka, N.; Sarma, J. C. Iodine as an acetyl transfer catalyst. *J. Chem. Res. Synop*. **1997**, 110.
9. Cope, A. C.; Herrich, E. C. Diethyl *cis*-Δ^4-tetrahydrophthalate and diethyl *cis*-hexahydrophthalate. *Org. Synth. Coll*. **1963**, *4*, 304.
10. Iqbal, J.; Srivastava, R. R. Cobalt(II) chloride–catalyzed acylation of alcohols with acetic anhydride: Scope and mechanism. *J. Org. Chem*. **1992**, *57*, 2001.
11. Li, A. X.; Li, T. S.; Ding, T. H. Montmorillonite K-10 and KSF as remarkable acetylation catalysts. *Chem. Commun*. **1997**, 1389.
12. Jin, T. S.; Ma, Y. R.; Zhang, Z. H.; Li, T. S. Sulfamic acid–catalysed acetylation of alcohols and phenols with acetic anhydride. *Synth. Commun*. **1998**, *28*, 3173.
13. Chauhan, K. K.; Frost, C. G.; Love, I.; Waite, D. Indium triflate: An efficient catalyst for acylation reactions. *Synlett* **1999**, 1743.
14. Saravanan, P.; Sungh, V. K. An efficient method for acylation reactions. *Tetrahedron Lett*. **1999**, *40*, 2611.
15. Chandrasekhar, S.; Ramachander, T.; Takhi, M. Acylation of alcohols with acetic anhydride catalyzed by $TaCl_5$: Some implications in kinetic resolution. *Tetrahedron Lett*. **1998**, *39*, 3263.
16. Pansare, S. V.; Malusare, M. G.; Rai, A. N. Magnesium bromide–catalysed acylation of alcohols. *Synth. Commun*. **2000**, *30*, 2587.
17. Ortia, A.; Tanahashi, C.; Kakuda, A.; Otera, J. Highly efficient and versetile acylation of alcohols with $Bi(OTf)_3$ as catalyst. *Angew. Chem., Int. Ed. Engl*. **2000**, *39*, 2877.
18. Claisen, L. Bemerkung zu einer Mittheilung von A. Deninger: Ueber Darstellung von Benzo und saureanhydridc. *Berichte der deutschen chemischen Gesellschaft* **1894**, *27*, 3182.
19. Schotten, C. Ueber die Oxydation des Piperidins. *Ber. Chem. Gesellsch*. **1884**, *17*, 2544.
20. Baumann, E. Ueber eine einfache Methode der Darstellung von Benzoësäureäthern. *Ber. Chem. Gesellsch*. **1886**, *19*, 3218.
21. (a) Hosseini Sarvari, M.; Sharghi, H. Zinc oxide (ZnO) as a new, highly efficient, and reusable catalyst for acylation of alcohols, phenols and amines under solvent free conditions. *Tetrahedron* **2005**, *61*(46), 10903; (b) Pasha, Md. A.; Manjula, K. TiO_2, a simple and an efficient catalyst for esterification of phenols under solvent-free condition. *Indian J. Chem*. **2008**, 47B(4), 597; (c) Kim, J. G.; Jang, D. O. Mild and efficient copper(II) oxide–catalyzed acylation of amines and alcohols. *Bull. K. Chem. Soc*. **2009**, *30*(7), 1435; (d) Murashige, R.; Hayashi, Y.; Ohmori, S.; Torii, A.; Yoko, A.; Muto, Y.; Murai, Y.; Oda, Y.; Hashimoto, M. Comparisons of O-acylation and Friedel–Crafts acylation of phenols and acyl chlorides and Fries rearrangement of phenyl esters in trifluoromethanesulfonic acid: Effective synthesis of optically active homotyrosines. *Tetrahedron* **2011**, *67*(3), 641; (e) Pasha, Md. A.; Reddy, M. B. M.; Manjula, K. Zinc dust, an extremely active and reusable catalyst in acylation of phenols, thiophenol, amines, and alcohols in a solvent-free system. *Eur. J. Chem*. **2010**, *1*(4), 385.
22. Simion, A. M.; Egashira, N.; Hashimoto, I.; Simion, C.; Mitoma, Y. O-Acylation of substituted phenols with various alkanoyl chlorides under phase-transfer catalyst conditions. *Synth. Commun*. **2012**, *42*(6), 921.

23. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry, 4th ed.*; ELBS: London, 1986.
24. Patil, V. D.; Rege, P.; Patil, J.; Dere, G. Efficient acylation and benzoylation of alcohols and phenols using cobalt nitrate under solvent-free condition. *IUP J. Chem.* **2010**, *3*(1), 42.
25. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Babaghanbari, M.; Zarea, M.; Shariati, L.; Taghavi, S. A. Zirconyl triflate: A new, highly efficient, and reusable catalyst for acetylation and benzoylation of alcohols, phenols, amines, and thiols with acetic and benzoic anhydrides. *J. Iran. Chem. Soc.* **2009**, *6*(3), 523.
26. Massah, A. R.; Toghyani, M.; Najafabadi, B. H. Green and efficient method for the acylation of amines and phenols in the presence of hydrotalcite in water. *J. Chem. Res.* **2012**, *36*(10), 603.
27. Verma, R. S.; Namboodiri, V. V. Solvent-free preparation of ionic liquids using a household microwave oven. *Pure Appl. Chem.* **2001**, *73*, 1309.
28. Braibante, H. T. S.; Braibante, M. E. F.; Rosso, G. B.; Oriques, D. A. Preparation of ß-enamino carbonylic compounds using microwave irradiation/K-10. *J. Braz. Chem. Soc.* **2003**, *14*, 994.
29. Kidwai, M. Dry media reactions. *Pure Appl. Chem.* **2001**, *73*, 147.
30. Caddick, S.; McCarroll, A. J.; Sandham, D. A. A convenient and practical method for the selective benzoylation of primary hydroxyl groups using microwave heating. *Tetrahedron* **2001**, *57*(29), 6305.
31. Marvi, O.; Fekri, L. Z.; Takhti, M. Montmorillonite K10 and KSF clays as acidic and green catalysts for effective esterification of phenols and alcohols under MWI. *Rus. J. Gen. Chem.* **2014**, *84*(9), 1837.
32. Chattopadhyay, G.; Chakraborty, S.; Saha, C. Brine-mediated efficient benzoylation of primary amines and amino acids. *Synth. Commun.* **2008**, *38*, 4068.
33. Basu, K.; Chakraborty, S.; Sarkar, A. K.; Saha, C. Efficient acetylation of primary amines and amino acids in environmentally benign brine solution using acetyl chloride. *J. Chem. Sci.* **2013**, *125*(3), 607.
34. Clarke, M. F.; Owen, L. N. Alicyclic glycols, part I: Toluene-p-sulphonyl and methanesulphonyl derivatives of cyclohexane-1:2-diol. *J. Chem. Soc.* **1949**, 315.