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RESEARCH ARTICLE

Heterogeneous CES Catalysed Acetylation and Allylation of Amines and Phenols

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ABSTRACT

Amines, naphthols and phenols are acylated using anhydrides by dissolving them in an aqueous medium containing catalytic ammount of calcinated egg Shell (CES). The present methodology is a green chemical process as the reactions is in a aqueous medium, convenient, efficient and environmentally benign with easy isolation of products and use of heterogeneous catalyst in aqueous medium. Allylation of 7-hydroxy-4-methyl-2H-chromen-2-one yields 7-(allyloxy)-4-methyl-2H-chromen-2-one catalysed by CES in polyethyleneglycol and allyl bromide.

KEYWORDS

Acetylation, Allylation, Amine, Calcinated Egg shell (CES), Heterogeneous Catalyst, Phenol

INTRODUCTION

Acetylation and allylation of alcohols, Amines and Phenols are an important and routinely utilized transformation in organic chemistry[1-3]. Knowing the importance of protection of hydroxyl and amine functional group during the multi-steps organic synthesis, the various methods for the protection of hydroxyl and amino groups of alcohols, phenols and amines using varieties of reagent and catalysts such as $HgCl_2$[4], Montmorillonite[5], TMS-Cl[6], $TaCl_5$-SiO_2[7], $ZnCl_2$[8], ZnO[9-10], Ru-catalyst[11], $Mg(ClO_4)$[12], SmI_2[13], $CeCl_3$[14], perchlorates[15], P_2O_5/Al_2O_3[16], $CoCl_2$[17-18], $ZrCl_4$[19], NH_2SO_3H[20], solid sup-ported HBF_4-SiO_2[21], lipase enzyme[22], $Al(OTf)_3$[23], $In(OTf)_3$[24], $Bi(OTf)_3$[25], polymer supported $Gd(OTf)_3$[26], $Ce(OTf)_3$[27], $Ag(OTf)_3$[28], molecular Iodine[29], nitro benzeneboronic acid[30], $NiCl_2$[31], $La(NO_3).6H_2O$[32], DCC[33], Co(II) salen-complex[34], Melamine trisulfonic acid (MTSA), ionic liquid, $ZnAl_2O_4$, have been reported, however, the most common acetylating reagents used are acetyl chloride, acetic acid, acetic anhydride or any other protic acid.

In spite of these ways of interest, due to the importance of acetylation and allylation Innovation of inexpensive and green catalyst is still in demand.

A variety of methods are now available for acetylation and allylation. Most of them have certain demerits such as use of expensive, toxic catalyst, long reaction times, harsh reaction conditions and non satisfactory yield of the desire products. With increasing environmental concerns and the regulatory constraints, the development of environmentally benign organic reactions has become a crucial and demanding

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area in modern organic chemical research. We wish to report a practical and convenient method for the preparation of amide, esters and allyl ether using Calcinated Egg Shell, a natural base catalyst.

The present research work described a highly efficient and eco-friendly protocol for acetylation under aqueous condition at room temperature using CES.

MATERIALS AND METHOD

Merck, pre-coated Silica gel 60 F_{254} (Aluminum sheets) plates were used for analytical TLC. IR spectra were recorded on FTIR spectrophotometer. ^1H NMR spectra were recorded (in $CDCl_3$ /DMSO-d^6) on 400 MHz spectrometer using TMS as an internal standard.

Preparation of Catalyst

Approximately 94% of a dry eggshell is calcium carbonate and has a typical mass of 5.5 grams[35]. Waste egg shells were collected and washed to remove the undesirable sticky material with plenty of water. Then placed the cleaned egg shell in the oven to dry completely. Crushed the dried egg shell in mortar and pestle to a fine powder. Then introduce the powder in muffle furnace to calcinate at 900^0C, after heating 2-3 hour thermal decomposition of Egg Shell (calcium carbonate) gives a white soft powder, calcinated egg cell (CES).

Charecterisation of catalyst by XRD: XRD of CES is compared with XRD of CaO which shows the formation of CaO from calcination of egg Shell.

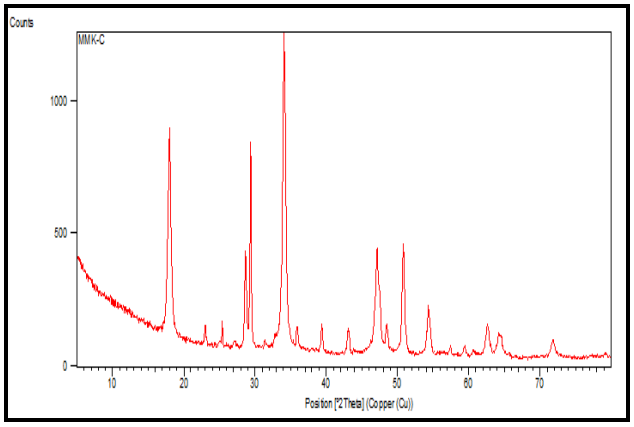


Figure 1: XRD of CaO

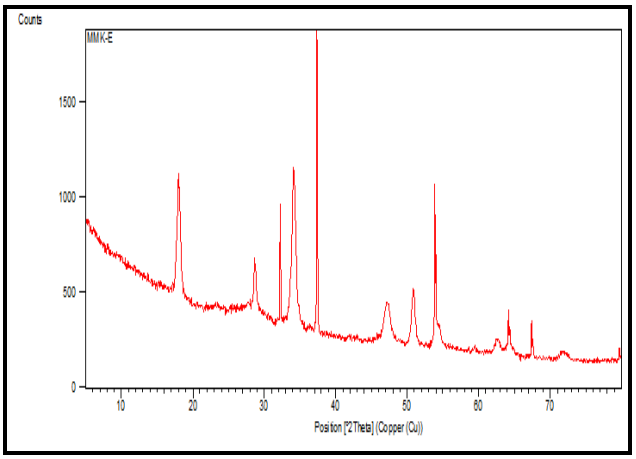


Figure 2: XRD of CES

N-phenylacetamide (1a)

Aniline 1 mmol was added into the water 5mL containing 25 mol% CES with constant stirring at room temperature. Add 2.5 mmol of acetic anhydride drop wise to avoid the complete hydrolysis of acetic anhydride with constant stirring. Completion of the reaction was monitored by TLC (ethylacetate:hexane = 30:70) seperated solid product was extracted with diethyl ether and recrastalyzed from hot distilled water.

IR (KBr, cm^{-1}): 3294, 3022, 2937, 1620, 1530, 1393.

^1H NMR (300 MHz, $CdCl_3$): δ 8.3 (S, 1H, exchangeable with D_2O), δ 7.5 (dd, 2H), δ 7.3-7.2 (m, 1H), δ 2.2 (S, 3H).

Elemental Analysis: C, 71.08; H, 6.70; N, 10.35; O, 11.86

Naphthalen-2-yl acetate (2f)

2-napthol 1 mmol was added into the water 5mL containing 25 mol% CES with constant stirring at room temperature. Add 2.5 mmol of acetic anhydride drop wise to avoid the complete hydrolysis of acetic anhydride with constant stirring. Completion of the reaction was monitored by TLC (ethylacetate:hexane = 30:70) seperated solid product was extracted with diethyl ether and recrastalyzed from hot distilled water.

IR (KBr, cm^{-1}): 3069, 1628, 1464, 1429, 1271

^{1}H NMR (300 MHz, $CdCl_3$): δ 7.8-7.7 (m, 3H), δ 7.5-7.4 (m, 3H), δ 7.2 (d, 1H), δ 2.3 (s, 3H)

Elemental Analysis: C, 77.41; H, 5.40; O, 17.16

7-(allyloxy)-4-methyl-2H-chromen-2-one (3a)

7-hydroxy-4-methyl-2H-chromen-2-one 1 mmol was added into the polyethyleneglycol 10mL containing 25 mol% CES then add 2.5 mmol of allyl bromide and reflux at 120^{0}C. Completion of the reaction was monitored by TLC (ethylacetate:hexane = 40:60) The reaction mixture was poured into crushed ice. The separated solid product was extracted with diethyl ether and recrastalyzed from ethanol.

IR:2997, 1604, 1226, 1689, 3230

^{1}H NMR (300 MHz, DMSOd^6): δ 2.5(s, 1H), δ 4.6 (dd, 2H), δ 5.3-5.7 (dd, 2H), δ 5.90 (m, 1H), δ 6.2 (s, 1H), δ 7.0 (d, 1H), δ 6.8 (d, 1H, J=8.7 Hz), δ 7.4 (d, 1HJ=8.1 Hz)

Elemental Analysis: C, 72.22; H, 5.58; O, 22.21

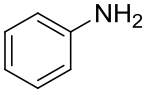
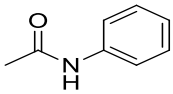
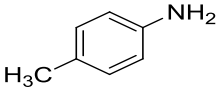
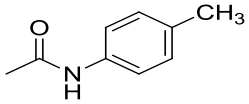
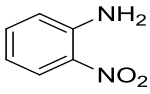
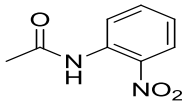
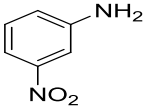
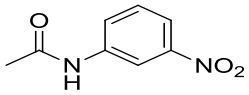
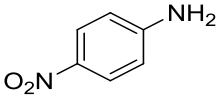
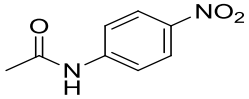
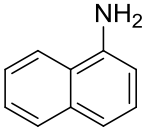
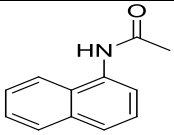
RESULTS AND DISCUSSION

The efficiency of CES in aqueous phase indicates formation of calcium hydroxide, which serves as active heterogeneous solid phase of catalyst as it is partially soluble in water. In the reported methodology Figure 3, the acetylation of β-napthol, m-nitroaniline and α-naphthylamine as a model reaction.

Treatment of these compounds with acetic anhydride in presence of CES catalyst yields the most satisfactory yield 99% in aqueous condition as depicted in the Table-1 and Table-2, In case of α-naphthol the reaction mixture was kept in the ice bath during the addition of acetic anhydride as the product form easily decomposes with increase in temperature.

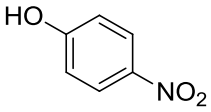
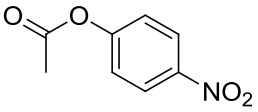
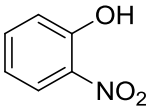
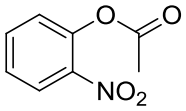
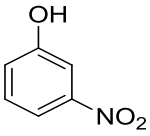
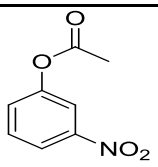
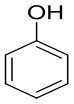
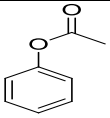
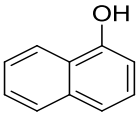
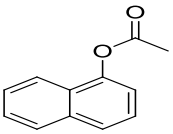
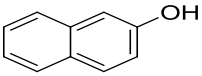
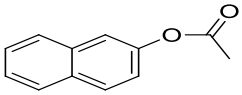
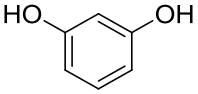
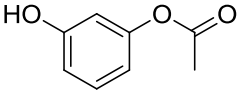
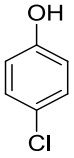
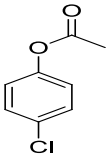
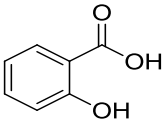
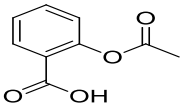
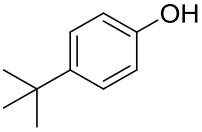
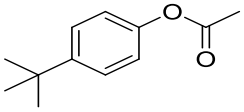
It was observed that phenol containing the electron withdrawing group underwent the reaction rapidly with good yield upto 98% as depicted in Table-2.

Table 1: N-Acetylation of Amines of amines

Sr. No.	Substrate	Product	Reaction time in min	[a]Yield %	Melting Point
1a.			10	96	112-114
1b.			08	98	149-150
1c.			12	89	90-92
1d.			11	[b]99	152-154
1e.			12	90	213-215
1f.			11	[b]99	155-157

[a]Yield Isolated, [b]Model reaction with 99% yield.

Table 2: O-acetylation of Naphthol and Phenol

Sr. No.	Substrate	Product	Reaction time in min	[a]Yield %	Melting Point
2a.			15	98	74-76
2b.			20	80	37-39
2c.			20	85	75-77
2d.			55	81	196
2e.			10	92	43
2f.			15	[b]99	67
2g.			30	85	283
2h.			20	86	231
2i.			NR	-	136
2j.			60	40	147-149

[a]Yield Isolated, [b]Model reaction with 99% yield

We have also carried out the allylation of 7-hydroxy-4-methyl-2H-chromen-2-one with allyl bromide in polyethylene glycol catalysed by CES at 120^0C which yields 7-(allyloxy)-4-methyl-2H-chromen-2-one Figure 2, Table-3.

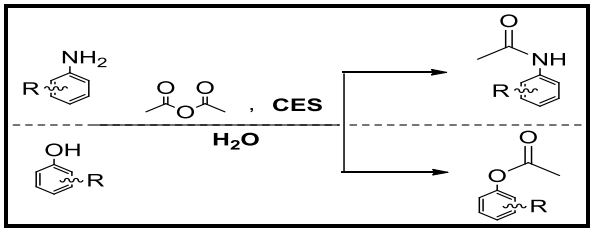
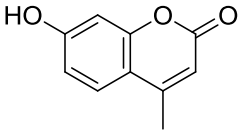
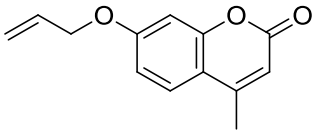
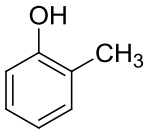
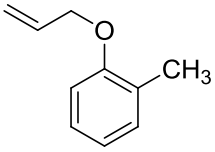
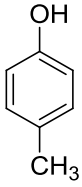
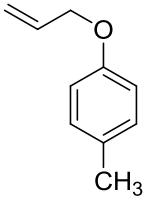
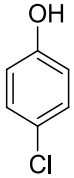
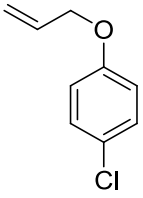


Figure 3: Acetylation of Amines and Phenols by CES in Water

CONCLUSION

In conclusion, we have shown that CES, is a efficient and environmentally benign catalyst for acetylation of amine, naphthol and Phenol. As egg Shell is made up of calcium carbonate after calcination calcium carbonate converted into calcium oxide. Partially soluble Calcium oxide in water give calcium hydroxide, which acts as a base. This work may increase interest among the researchers and inspire them about the use of CES as a base catalyst in organic transformations.

Table 3: O-allylation of Phenol using acetic anhydride and CES

Sr. No.	Substrate	Product	Reaction time in min	[a]Yield %	Melting Point
3a.			60	85	210
3b.			60	69	[b]205
3c.			60	71	[b]215
3d			45	79	[b]230

[a]Yield Isolated, [b]Boiling Point

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