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Eggshell Waste : An Efficient Solid Catalyst for the Synthesisof 5-Arylidene Barbituric Acids under Solvent-Free Condition

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ABSTRACT

Efficient synthesis of 5-arylidene barbituric acid derivatives in presence of chicken eggshell waste at room temperature with grinding has been reported. Biologically active 5-arylidene barbituric acid derivatives were obtained in high yields (88-96 %) in a short reaction time (2-7 min) under solvent-free condition. This method has advantages such as avoidance of the organic solvents, short reaction times and production of pure products without any by product.

Keywords : Chicken eggshell waste, 5-Arylidene barbituric acid derivatives, Green catalyst, Grinding, Solvent free condition.

I. INTRODUCTION

Derivatives of barbituric acids have been widely used as anaesthetic, sedative, anticonvulsant, hypnotic, antitumor agents and antiosteoporosis[1].The 5-Aryl-pyrano pyrimidine-2, 4-diones obtained from 5-arylidene barbituric acids has biological activities like antibacterial[2], antiviral[3], prostate-protective[4]and antifungal[5]. Arylidene barbituric acids are useful as intermediates in synthesis of benzyl barbituric derivatives[6], unsymmetrical derivatives[7]and loxadiazaflavines[8]. Recently some of them have been used as dyes[9].A 5-arylidene barbituric acids can be considered as models of redox coenzymes such as FAD, NAD and used as oxidants for mild oxidation of thiols[7, 10] and alcohols[11].

Various methods have been reported for the synthesis of 5-arylidene barbituric acid derivatives like amino sulfonic acid[12], microwave irradiation[13],$CoFe_2O_4$ nanoparticles[14], ionic liquid[15],infra-red promoted[16], nickel nanoparticles[17], $LaCl_3.7H_2O$[18] and various acid-base catalyzed condensation reactions[19-22].However, many of these methods suffer from the drawbacks of green chemistry[23]. Therefore the eco-friendly, heterogeneous, clean process and green catalysts which can be recycled are under permanent attention. The solvent-free reaction represents very powerful green chemical procedure from both economical and synthetic point of view.

In continuation to our ongoing research on the synthesis of heterocyclic molecules using nanoparticles as a catalyst[24-29]and to explore the importance of chicken eggshell waste as a catalyst in organic synthesis[30], hereinwe wish to report a simple synthesis of 5-arylidene barbituric acid derivatives using chicken eggshell wasteas reusable catalyst under solvent-free conditions with grinding at room temperature.

II. EXPERIMENTAL SECTION

Preparation of chicken eggshell waste catalyst

The waste chicken eggshell was collected, washed and dried at room temperature. The eggshell was crushed and grind by mortar and pestle. The fine

powder was dried at 150°C in heating oven and used as catalyst in reaction.

Synthesis of 5-arylidene barbituric acid derivatives

Aromatic aldehydes **1** (1.0 mmol) and barbituric acid **2** (1.0 mmol) were mixed with chicken eggshell waste as a catalyst (0.040 g) in a mortar at room temperature. The reaction mixture was grounded and reaction was monitored by TLC. The solid residue was dissolved in hot ethanol and filtered off. The catalyst was separated by filtration. The crude product was collected from filtrate after cooling to room temperature and recrystallized from ethanol to give products **3** (**a-i**). The spectral data IR, ^{1}H NMR, ^{13}C NMR and MS of all synthesized compounds are reported.

5-Benzylidene barbituric acid (Table II, entry 3a**)**: m. p. 263°C; IR (KBr): 3459, 3219, 3062, 1747, 1565 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.22 (s, 1H), 11.10 (s, 1H), 10.58 (s, 1H), 8.33-8.27 (m, 3H), 6.85 (d, 2H, *J*=7.10 Hz);^{13}C NMR (100 MHz, DMSO-d_6): δ 163.6, 162.2, 155.7, 150.4, 133.7, 133.3, 132.4, 128.3, 119.2; M. F: $C_{11}H_8N_2O_3$; M. W: 216; MS (*m/z*): 217 $(M+1)^+$.

5-(4-Chlorobenzylidene) barbituric acid (Table II, entry 3b**)**: m. p. 299°C; IR (KBr): 3430, 3214, 3087, 1752, 1675, 1578, 1090 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.37 (s, 1H), 11.20 (s, 1H), 8.24 (d, 2H, *J*=8.0 Hz), 8.07 (s, 1H), 7.51 (d, 2H, *J*=8.0 Hz);^{13}C NMR (100 MHz, DMSO-d_6): δ 163.6, 162.1, 153.4, 150.1, 137.5, 135.3, 132.1, 128.3, 120.2; M. F: $C_{11}H_7ClN_2O_3$; M. W: 251; MS (*m/z*): 252 $(M+1)^+$.

5-(4-Methylbenzylidene) barbituric acid (Table II, entry 3c**)**: m. p. 279°C; IR (KBr): 3490, 3350, 3092, 1729, 1679, 1658, 1574 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.43 (s, 1H), 11.26 (s, 1H), 8.34 (s, 1H), 8.13-7.38 (m, 4H), 2.15 (s, 3H);^{13}C NMR (100 MHz, DMSO-d_6): δ 163.8, 162.1, 155.7, 150.6, 143.8, 134.5, 130.2, 129.4, 118.1, 21.6; M. F: $C_{12}H_{10}N_2O_3$; M. W: 230; MS (*m/z*): 231 $(M+1)^+$.

5-(4-Bromobenzylidene) barbituric acid (Table II, entry 3d**)**: m. p. 293°C; IR (KBr): 3495, 3360, 3090, 1737, 1672, 1561 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.41 (s, 1H), 11.24 (s, 1H), 8.24 (s, 1H), 8.01-7.77 (m, 4H);^{13}C NMR (100 MHz, DMSO-d_6): δ 165.11, 160.2, 153.2, 150.2, 134.5, 131.8, 131.1, 127.6, 119.7; M. F: $C_{11}H_7BrN_2O_3$; M. W: 295; MS (*m/z*): 296 $(M+1)^+$.

5-(4-Hydroxybenzylidene) barbituric acid (Table II, entry 3e**)**: m. p. >300°C; IR (KBr): 3542, 3418, 3260, 3080, 1742, 1660, 1581, 1527, 1281 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.22 (s, 1H), 11.10 (s, 1H), 10.58 (s, 1H), 8.33-8.27 (m, 3H), 6.85 (d, 2H, *J*=8.80 Hz);^{13}C NMR (100 MHz, DMSO-d_6): δ 164.01, 163.16, 162.02, 156.25, 150.09, 138.57, 123.65, 115.37, 113.45; M. F: $C_{11}H_8N_2O_4$; M. W: 232; MS (*m/z*): 233 $(M+1)^+$.

5-(3-Nitrobenzylidene) barbituric acid (Table II, entry 3f**)**: m. p. 246°C; IR (KBr): 3442, 3240, 3095, 1780, 1697, 1596, 1537, 1435 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.45 (s, 1H), 11.30 (s, 1H), 8.90 (s, 1H), 8.34 (s, 1H), 8.31-8.28 (m, 1H), 8.23-8.21 (m, 1H), 7.73 (t, 1H, *J*=8.0 Hz);^{13}C NMR (100 MHz, DMSO-d_6): δ 165.0, 162.4, 152.3, 150.4, 150.1, 145.0, 135.0, 133.4, 132.4, 131.2, 118.1; M. F: $C_{11}H_7N_3O_5$; M. W: 261; MS (*m/z*): 262 $(M+1)^+$.

5-(4-Nitrobenzylidene) barbituric acid (Table II, entry 3g**)**: m. p. 294°C; IR (KBr): 3323, 3242, 3095, 1742, 1692, 1596, 1517 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.46 (s, 1H), 11.30 (s, 1H), 8.31 (s, 1H), 8.23 (d, 2H, *J*=8.70 Hz), 8.01 (d, 2H, *J*=8.70 Hz);^{13}C NMR (100 MHz, DMSO-d_6): δ 165.2, 162.0, 157.3, 150.2, 136.4, 136.2, 135.1, 134.4, 118.1; M. F: $C_{11}H_7N_3O_5$; M. W: 261; MS (*m/z*): 262 $(M+1)^+$.

5-(4-Methoxybenzylidene) barbituric acid (Table II, entry 3h**)**: m. p. 277°C; IR (KBr): 3401, 3233, 3094, 1712, 1672, 1546, 1206 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.32 (s, 1H), 11.17 (s, 1H), 8.30 (s, 1H), 8.12-7.35 (m, 4H), 3.84 (s, 3H);^{13}C NMR (100 MHz, DMSO-d_6): δ 164.4, 163.6, 162.7, 155.2, 150.2, 137.5, 125.4, 115.7, 114.2, 56.2; M. F: $C_{12}H_{10}N_2O_4$; M. W: 246; MS (*m/z*): 247 $(M+1)^+$.

5-(2-Chlorobenzylidene) barbituric acid (Table II, entry 3i**)**: m. p. 253°C; IR (KBr): 3360, 3230, 3075, 1732, 1657, 1547 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ 11.56 (s, 1H), 11.29 (s, 1H), 8.33 (s, 1H), 7.77 (d, 1H, *J*=7.60 Hz), 7.72 (d, 1H, *J*=7.60 Hz), 7.49 (d, 1H,

J=7.60 Hz), 7.38 (d, 1H, *J*=7.60 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.7, 161.1, 150.9, 150.1, 133.6, 132.4, 132.1, 130.9, 129.4, 126.7, 122.3; M. F: $C_{11}H_7ClN_2O_3$; M. W: 251; MS (*m/z*): 252 $(M+1)^+$.

III. RESULTS AND DISCUSSION

The reaction between benzaldehyde **1** (1.0 mmol) and barbituric acid **2** (1.0 mmol) was used as a model reaction to optimize the amount of catalyst (**Scheme**). It was found that 0.040 g ofchicken eggshell wastewas the appropriate quantity of the catalyst to offer the reaction (**Table I**). All reactions were performed by grinding method at room temperature. The reactions were completed within 2-7 min with excellent product yields (88-96 %). A blank reaction of benzaldehyde and barbituricacid was performed to confirm the effectiveness of chicken eggshell wasteduring this reaction. In absence of chicken eggshell waste, the reaction was incomplete even after 9 hrs.

After optimizing the reaction conditions, a variety of aromatic aldehydes with barbituric acid were employed under reaction conditions to evaluate the scope of this reaction. A series of 5-arylidene barbituric acid derivatives **3(a-i)**were prepared by using chicken eggshell wasteas a catalyst (**Table II**) with excellent yields (88-96 %) at room temperature. The reactions proceeds smoothly and no undesirable side reactions were observed. The nature of substituents on the aromatic ring does not affect on the condensation reaction. The condensation reactions of aromatic aldehydes carrying electron-donating or electron-drawing groups were also successfully carried out with this method in excellent yields and short reaction times.

In view of eco-friendly procedure, the catalytic efficiency of chicken eggshell wastewas also checked by its recovery and reusability. It was found that catalyst showed good results after four successive runs. It shows the same activity as fresh catalyst without any significant loss in its activity (**Table III**).

Table I. Effect of catalyst

Entry	Amount of catalyst (g)	Time (min)	Yield(%)
1	0.010	5	87
2	0.020	4	89
3	0.030	3	91
4	0.040	2	92
5	0.050	2	92
6	0.060	2	92

Table II.Synthesis of 5-Arylidene barbituric acid derivatives using chicken eggshell waste

Entry	Products (R group)	Time (min)	Yield(%)
3a	H	2	92
3b	4-Cl	3	94
3c	4-CH_3	7	93
3d	4-Br	2	95
3e	4-OH	3	96
3f	3-NO_2	4	88
3g	4-NO_2	2	94
3h	4-OCH_3	3	89
3i	2-Cl	3	90

Table III.Recycling of catalyst

Cycles	Yield(%)
Initial	92
1	92
2	91
3	89
4	88

IV. CONCLUSIONS

In this study chicken eggshell wasteas an efficient solid catalyst for the synthesisof biologically active 5-arylidene barbituric acid derivatives with grinding method under solvent-free condition has been described. The present method offers significant advantages such as simple work up, shorter reaction times, excellent yields, environmentally benign, grinding method, solvent-free reaction condition and reusability of catalyst, this protocol is economic and eco-friendly.

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