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Efficient and Facile One-Pot Synthesis of Novel Benzimidazoles using Rice Husk

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Efficient and Facile One-Pot Synthesis of Novel Benzimidazoles using Rice Husk

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Abstract- New and facile one-pot approach for the synthesis of substituted benzimidazoles from the reaction of substituted benzaldehyde and o-phenylenediamine room temperature using Rice Husk Ash: CaCl₂ (RHA:CaCl₂) as a green catalyst was presented in the paper. After the completion of the reaction, the reaction mixture was poured into ice-cold water with stirring, and the precipitated product was filtered using the filter pump. The crude product was then recrystallized from ethanol to give analytically pure samples in good to excellent yield. The purity of compounds were characterized by melting point and thin-layer chromatography. The synthesized compounds were characterized by using ¹H NMR and FTIR spectral techniques. Metal-free, short reaction time, high yields, mild reaction condition, simple work-up, high atom economy, cost-effectiveness, and no need for column purification are some beauties of this methodology.

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I. INTRODUCTION

In recent years, the progress of science and technology gradually shifted more towards environmentally benign, sustainable, and green resources. In this series, much attention has been focused on the utilization of plant biomass as biocatalyst. Amongst the various biomasses, with abundant and renewable energy sources, rice husk is not only a potential source of energy but also a value-added by-product [1]. In the last days, there were many reasons associated with rice husk for not being effectively like (i) lack of awareness of its potential by farmers and industry persons, (ii) socio-economic problems, (iii) penetration of technology, (iv) lack of environmental concern and many others. The only solution to these problems associated with the utilization of this solid waste needs to be detected both in quality and quantity aspects. Benzimidazole and its derivatives have reported the number of biological importance like they can be used as anticonvulsant, antibacterial, antifungal, antitumor, anthelmintic, ant amoebic, analgesic, and antiulcer [2-3]. Recent results indicate that the benzimidazole structure can bind in the DNA minor groove and can act as a ligand to transition metals. So, it must be necessary to develop a mild and easy procedure for the synthesis of these bioactive chemicals. Generally, benzimidazoles were prepared by

CAN [4], microwave-assisted [5], lead peroxide [6]. Despite of these methods, polycondensation of o-phenylenediamine with aryl aldehydes is more efficient and facile. Recently, some of the green protocol for the synthesis of benzimidazole derivatives has been carried out, such as the use of pectin in water [7]. In continuation of these series, we want to explain the applicability of RHA:CaCl₂ as a newly reported green catalyst which is reusable many times without loss of activity and performs the reaction under mild conditions with high yields.

II. EXPERIMENTAL DETAILS

The contents of rice husk are hemicellulose 24.3%, cellulose 34.4%, lignin 19.2%, ash 18.85% and the other substances are 3.25% [8]. Cellulose and lignin did not show the bonding properties because these are mostly inert but the monomeric components of hemicelluloses such as methyl glucuronic acid (monosaccharides), which become polar due to the electrometric effect of carboxylic acidic part. The active acidic monosaccharide can be extracted by removing lignin and cellulose from rice husk with an alkaline metal treatment [9]. All reagents and solvents were used in analytical grade and used without purification. Melting points were determined in open capillaries on a Ganson electric melting point apparatus and are uncorrected. Infrared spectra (4000-350 cm⁻¹) of the synthesized compounds were recorded in KBr pellets on Perkin Elmer FT-IR-R2X spectrophotometer, and frequency was expressed in cm⁻¹. The ¹H NMR spectrum was recorded in CDCl₃ or DMSO-*d*₆ using tetra methyl silane as internal reference on "Brucker Ac 400 F" (400 MHz) nuclear magnetic resonance spectrometer. The chemical shift values were quoted in delta (ppm).

a) General procedure of the synthesis of biocatalyst

The catalyst was prepared by sorption of an aqueous solution of CaCl₂·2H₂O (7.35 gm, 0.05 mmol) in per mL distilled water on rice husk (0.25 gm). The mixture was heated at 100 °C for 4 hours to give RHA:CaCl₂ [9].

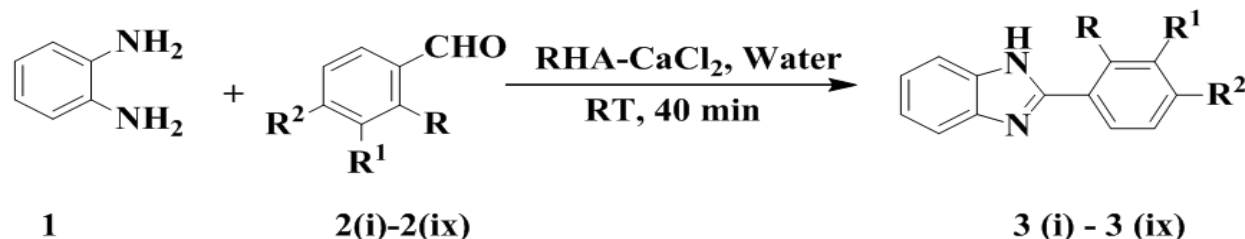
b) General procedure of the synthesis of benzimidazole

O-phenylenediamine (20 mmol) was added to a mixture of RHA:CaCl₂ (20 mg), substituted aldehydes (20 mmol), and 10 mL distilled water. Thus the resulting mixture was stirred at room temperature for 40 min. The progress of reaction was monitored by thin-layer

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chromatography (Ethyl acetate: n-hexane 2:8). After completion of the reaction, the mixture was workup by the addition of ice-cold water. The yellow solid products was separated by simple filtration and recrystallized from ethanol. If the product was gummy, it was extracted with ethyl acetate, and the organic phase was washed with water and dried over sodium sulfate. The

Chemical reaction



Scheme-1

III. RESULT AND DISCUSSION

The model reaction between salicylaldehyde 2(i) (2.44g; 20mmoles) and o-phenylene diamine(1) (3.74g; 20mmoles) in the presence of RHA.CaCl₂ was taken in the flask and stirred for 40 min on the magnetic stirrer. The solid that separated and worked up with cold water and recrystallized from ethanol to furnish 3(i) as the product in quantitative yield (Table 3, Entry 1). Inspired by this result, the concentration of catalyst was optimized through the above reaction by using different amounts of catalyst i.e. 0.12, 0.25, 0.50, 0.75, 1.00 gm (Table 1, Entry 1-5) of RHA.CaCl₂ in the water at room temperature for 40 min to give the desired products 3(i). The reaction procedure was performed in the absence of catalyst at the same condition; a low yield is obtained, which shows the value of the prescribed agitator. Fig.1a shows SEM images of untreated rice husk; this figure represents an irregular shape of fibers and rough surface; but a smooth and regular form was showed after treatment with hydrated calcium chloride (CaCl₂.2H₂O). At low magnification, RHA.CaCl₂(Fig 1b, c) shows a regular surface, but the shape of fiber particles does not appear accurately. But at high magnification RHA.CaCl₂(Fig. 1d) seems to be composed of regular-shapedp articles with a uniform distribution of CaCl₂ on the surface. Due to this, calcium treatment improves the fiber surface and bond uniqueness by removing hemicelluloses and producing regular surface. This topography offers better fiber-matrix interface bond and an increase in mechanical properties. Treatment by alkali and alkaline reduces the lignin and hemicellulose content in natural fibers, increases the surface area, allowing the dissemination of water molecules to the inner layers, and breaks the bonds between lignin-carbohydrate and hemicellulose [17].

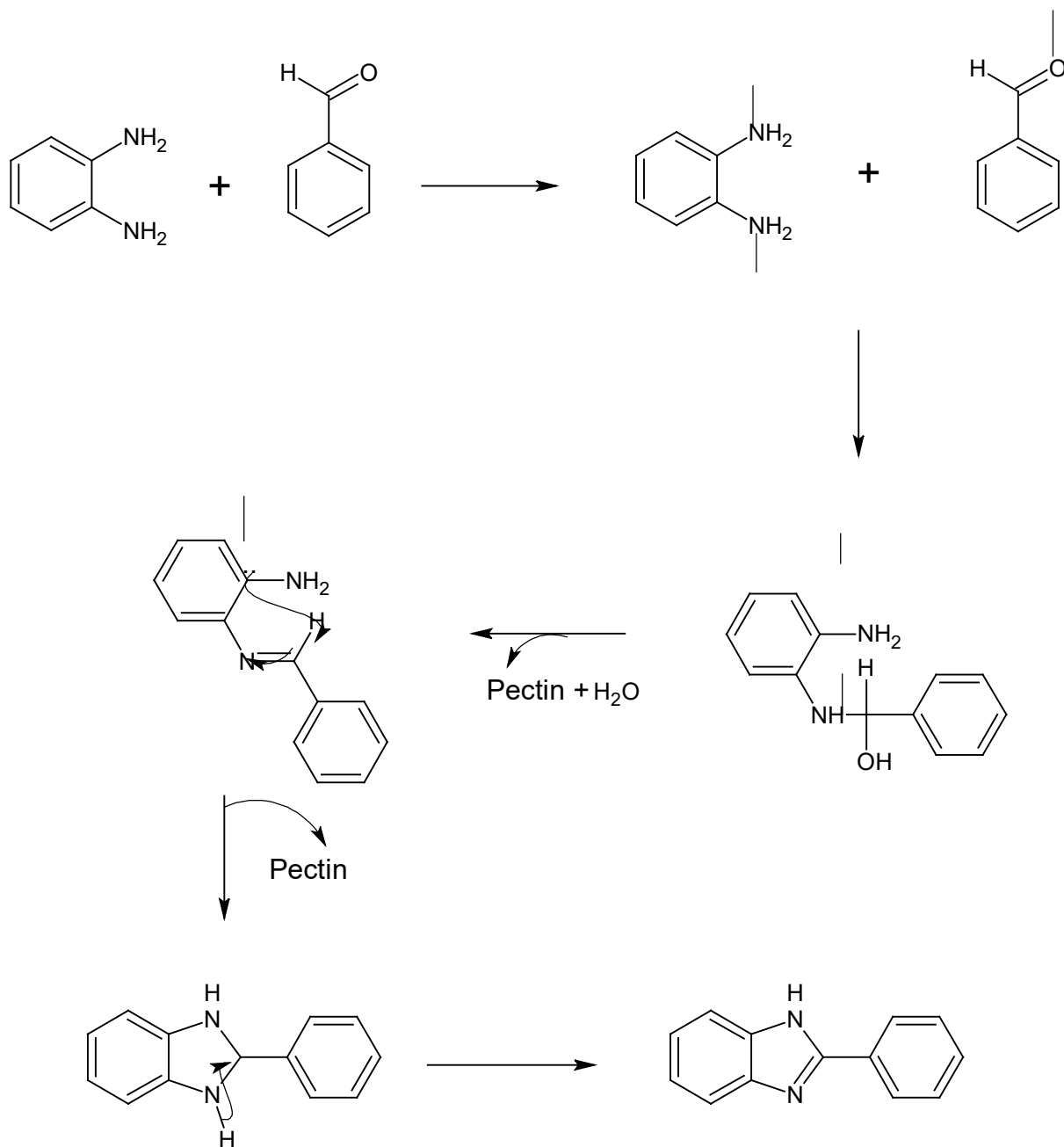
reaction was found to complete within 40 min to give 2-(1*H*-benzimidazole-2-yl) phenol 3(i) a product in quantitative yield (Table 3, entry 1). Various derivatives of benzimidazole and their yield formed was shown in Table 2 under (Scheme-1). Also, the speciality of the catalyst in comparison of other is shown in Table 3.

a) Catalyst recycles

Reusability is one attractive advantage of green catalysts. A recycling experiment was conducted using the above-mentioned model reaction (Scheme 1). The syntheses were performed three times and the effect of recycling catalysts on yields of 3(i), as shown in Table 2. In every cycle, the catalyst was almost quantitatively recovered, and after second and third-time use of catalyst, the decreasing yield is not much more significant.

b) Plausible Mechanism for Synthesis of Benzimidazole in the presence of RHA. CaCl₂

The possible mechanism for the synthesis of benzimidazole (Scheme 1) depicted below. The reaction proposed that the aryl aldehyde was first activated by green catalyst by nucleophilic attack on carbonyl group, then o-phenylene diamine attacks the activated carbonyl group of the compound, which leads to the formation of the intermediate and intermolecular cyclization proceeds to form the desired product.

RHA.CaCl₂

c) Spectral data of some selected compounds

- 2-(1H-benzimidazol-2-yl)phenol*: pale yellow solid. mp: 293–296°C; ¹H NMR (400 Hz, CDCl₃): δ 3.62 (brd, 1H, OH); 7.30-8.91(m, 8H, Ar-H); 10.38 (s, 1H, NH); IR (KBr) cm⁻¹:3366 (OH), 3165 (N-H), 3035(C=CH), 1618 (C=C, aromatic)
- 2-(2-chlorophenyl)-1H-benzimidazole*: pale yellow solid. mp: 225–226°C; ¹H NMR (400 Hz, CDCl₃):δ6.97-8.24 (m, 8H, Ar-H), 11.01 (s, 1H, NH);IR (KBr) cm⁻¹:3261 (N-H), 3030(C=CH), 1596 (C=C, aromatic), 754 (C-Cl)
- 2-(3-nitrophenyl)-1H-benzimidazole*: pale yellow solid. mp: 164-186°C; ¹H NMR (400 Hz, CDCl₃): δ 6.12-8.28 (m, 8H, Ar-H), 10.33 (s, 1H, NH); IR (KBr) cm⁻¹: 3326 (N-H), 2968 (C=CH), 1590 (C=C, aromatic), 1318 (NO₂)

d) *Comparison of the results of the present methods for the synthesis of benzimidazoles with the reported methods*

Table 4 indicates the comparison of the activity of different catalysts by considering the yield of the reaction. We observed that the RHA.CaCl₂ gives catalytic activity in terms of product yield, solvent, and response time of reaction compared to other catalysts in the literature such as CAN, p-TsOH, Metal-Nitrate, Ammonium Chloride, Ring-Closing. RHA.CaCl₂ is a readily available and inexpensive biocatalyst, which makes this method green and mild. Also the above catalyst is a renewable catalyst that follows one of the green chemistry principles regarding the maximum yield of renewable resources.

IV. CONCLUSION

In summary, we have developed an efficient catalytic system for the synthesis of substituted benzimidazoles by using rice husk. Under the improved method, it offers several benefits over the previous methods, which includes the elimination of toxic chemicals, cheap, and the main product was obtained in good to excellent yields. Furthermore, the rice husk catalytic system could be reuse up to three times without significant loss of activity. All synthesized compounds were obtained by precipitation without the need for column purification. This current improved method is capable of minimizing the use of hazardous chemicals and, at the same time, provides an alternative way of bio-waste management. We predict that the current procedure will provide a great utility in the synthesis of other heterocyclic compounds shortly.

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Figures

Graphical Abstract:

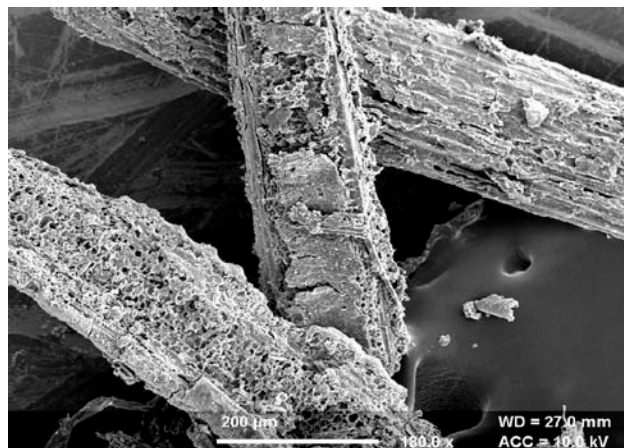
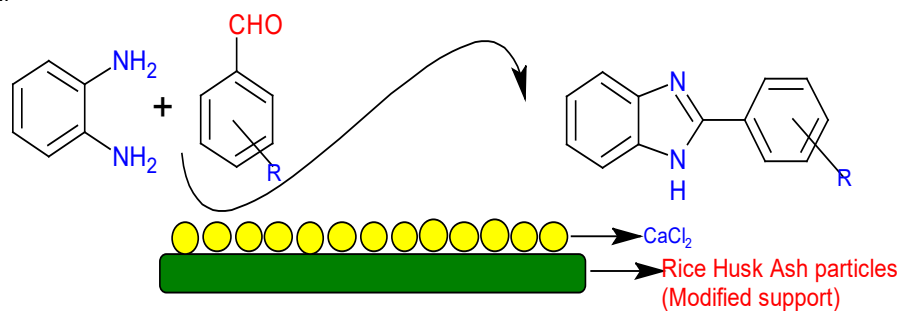
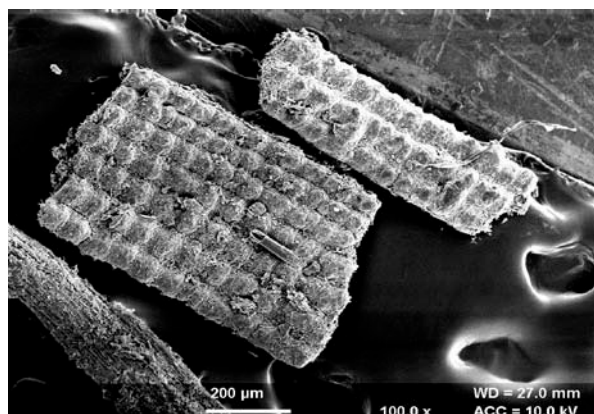
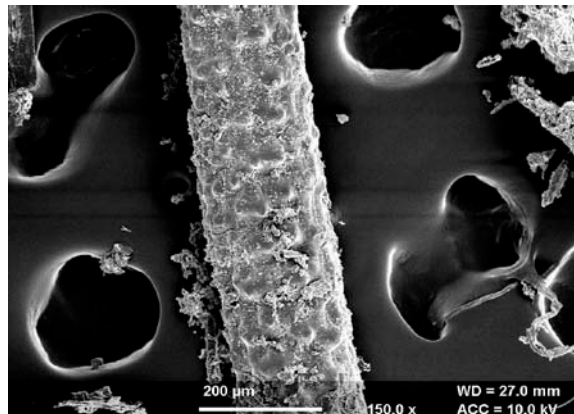


Fig.: 1a SEM Images of untreated Rice Husk

Fig.: 1b, c SEM of RH.CaCl₂ at low magnification

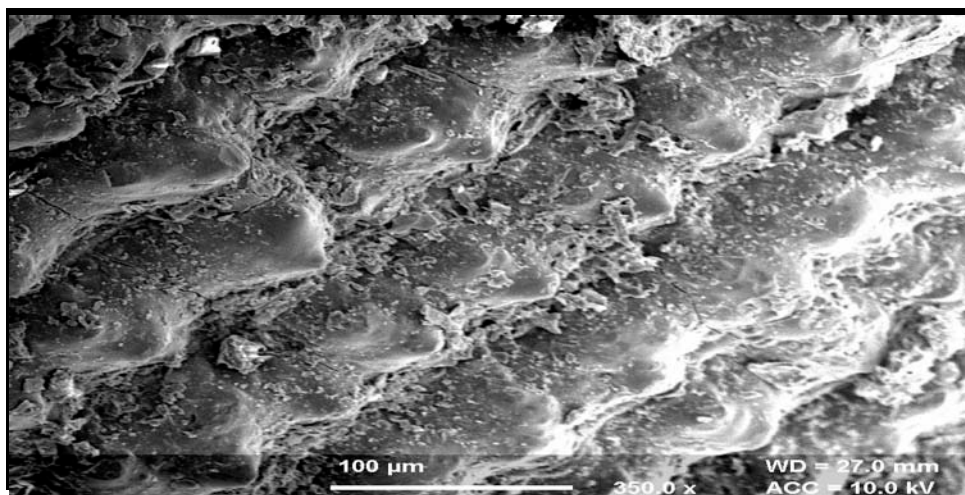


Fig.: 1d SEM of RHA.CaCl₂ at high magnification

Tables

Table 1: Screening of RHA.CaCl₂ for the synthesis of 3(i)

Entry	Amount of Catalyst (gm)	Time (min)	Yield
1.	0.12	75	79
2	0.25	40	82
3	0.50	30	80
4	0.75	25	76
5	1.00	25	76

Entry 2 is the best concentration for the prescribed catalyst

Table 2: Reusability of catalyst

Reuse Cycle	Fresh	First	Second	Third
Time (min)	40	40	60	90
Yield (%)	82	82	78	76

Table 3: Synthesis of benzimidazoles in presence of RHA.CaCl₂

Entry	R	R ¹	R ²	Product	Yield	Phase	Mpt. (°C) [Ref]
1	OH	H	H	3(i)	82	Solid	180-182 [10]
2	H	OH	H	3(ii)	92	Solid	282-284 [11]
3	Cl	H	H	3(iii)	88	Solid	225-226 [10]
4	CH ₃	CH ₃	H	3(iv)	86	Gummy	-----
5	H	OH	OH	3(v)	90	Gummy	-----
6	H	NO ₂	H	3(vi)	84	Solid	164-186 [10]
7	H	H	OCH ₃	3(vii)	90	Solid	223-225 [10]
8	H	H	OH	3(viii)	82	Solid	285-287 [11]
9	H	H	Cl	3(ix)	78	Solid	294-296 [10]

Table 4: Comparison of the results with the reported methods

S. No.	Catalyst	Solvent	Temperature (°C)	Time (min)	Yield (%)	Literature
1	CAN	PEG	50	120	90	[4]
2	<i>p</i> -TsOH	DMF	80	10	82	[12]
3	Metal-Nitrate	Methanol	RT	30	80	[13]
4	Ammonium Chloride	Ethanol	80-90	120	78	[14]
5	Ring-Closing	Ethanol	90	120	78	[15]
7	RHA.CaCl ₂	Water	RT	40	82	Present work