Vol 7 Issue 2 Nov 2017

ISSN No : 2249-894X

Monthly Multidisciplinary Research Journal

Review Of Research Journal

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RNI MAHMUL/2011/38595 **ISSN No.2249-894X**

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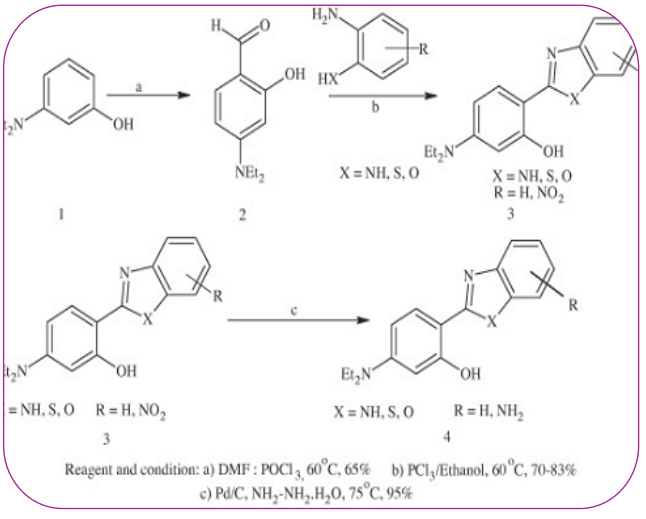
REVIEW OF RESEARCH
ISSN: 2249-894X
IMPACT FACTOR : 5.2331(UIF)
VOLUME - 7 | ISSUE - 2 | NOVEMBER - 2017

SIMPLE TWO COMPONENT CONDENSATION FOR EFFICIENT SYNTHESIS OF 2-(2'-HYDROXYPHENYL) BENZIMIDAZOLE



Mansing M. Mane
Assit. Professor, R.B.Madkholkar Mahavidyalaya, Chandgad, Dist. Kolhapur,, India.

ABSTRACT: -

We investigated a simple strategy for synthesis of 2-(2-hydroxyphenyl) benzimidazole from two component condensation of salicylaldehyde, and o-phenylene diamine in ethanol medium at room temperature. Mild reaction conditions, short reaction time at ambient temperature, use of eco-friendly solvent system, simple work-up procedure, no chromatographic separation are of present protocol.

KEYWORDS: *Salicylaldehydes, o-phenylene diamine, Sulphamic acid, RT, Ethanol.*

INTRODUCTION:

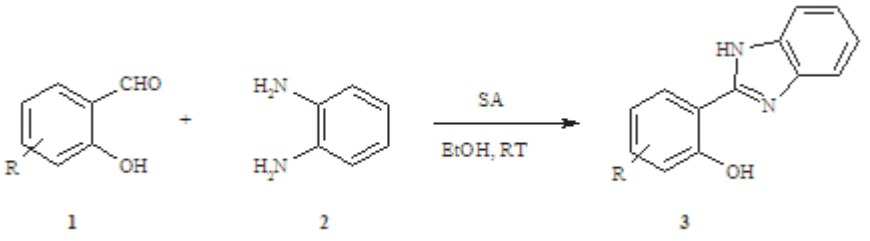
Benzimidazole posses broad-spectrum fungicides and have been used commercially for the control of plant diseases [1] since the late 1960's. Derivatives of benzimidazole get attraction due to their interesting pharmacological activities such as antiallergic[2], antihelminthic[3] , antiviral and antitumor[4], antimicrobial[5], CNS receptor[6], anti-HIV[7], anticancer[8], cytotoxic[9] and anti-inflammatory[10,11]. Benzimidazole derivatives can also be acts as proton pump inhibitors, which leads for the discovery of important drugs like omeprazole, lansoprazole, rabeprazole, and pantoprazole. Among derivatives of benzimidazole,2-(2-hydroxyphenyl) benzimidazole(HPBI), shows interesting emission properties via excitated state intramolecular proton transfer (ESIPT) and proved to be new series of fluorescent probes [12]. HPBI reported as tunable laser dye and corresponding oxazole and thiazole find potential applications in nonlinear optics and light emitting devices[13-15].

Although various method have been reported in the literature for the synthesis of benzimidazole derivatives[16], surprisingly very few method are reported for the synthesis of HPBI[17,18], which restricted to harsh reaction condition involving longer duration and limited substrate scope. So search for simple protocol involving easily available starting materials, cost effective catalyst, rapid, safer solvent and applicable to formation of variety of derivatives is need of current scenario. Non hygroscopic, cost effective, readily available Sufamic acid (SA) emerged as effective bronsted acid catalyst for organic transformation in recent years. Our earlier experience working with Sulphamic acid[19a-c] and interesting emission properties of HPBI, provoke us in the synthesis and study of emission properties of derivatives of HPBI.

RESULT AND DISCUSSION

Initially we carried out two component condensation of salicylaldehyde and o-phenylene diamine(OPD) under different acidic conditions (Table 1). Results of our study reveals that among employed catalyst, sulfamic acid and EPZ 10 clay catalyst shows good results in terms of isolated yields. Major problem we face with EPZ10 catalyst is tedious workup

procedure and use of organic solvent. Where as, sulfamic acid as it is water soluble can be easily removed, it's commertial availability and low cost made us to choose sulfamic acid as catalyst for current transformation. Catalyst loading shows 20 mole % of sulfamic acid is enough to give high isolated yield of HPBI.



Scheme 1: Synthesis of 2(2'-hydroxy phenyl) benzimidazole

Table1: Screening of catalysts for synthesis of 2(2'-hydroxy phenyl) benzimidazole

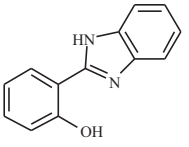
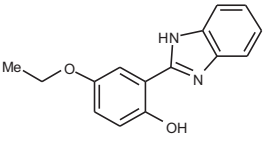
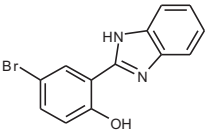
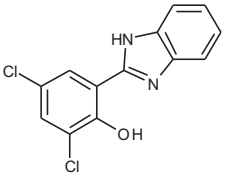
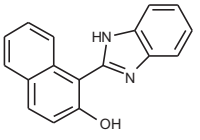
Entry	Catalyst	Mole %	Solvent/condition	Time min	Yield % [a]	Reff.
1	No catalyst	-	EtOH/RT	120	NC	This work
2	pTSA	20	EtOH/RT	60	75	This work
3	$AlCl_3$	20	EtOH/RT	60	74	This work
4	EPZ 10	20	$CHCl_3$/RT	30	85	This work
5	EPZ-G	20	$CHCl_3$/RT	60	65	This work
6	TFA	20	EtOH/ Reflux	overnight	38	[18]
7	Zirconium oxychloride	20	Solvent free/MW	6 min	65	[17]
8	**SA**	**20**	**EtOH/RT**	**30**	**85**	This work
9	SA	05	EtOH/RT	30	70	This work
10	SA	10	EtOH/RT	30	73	This work
11	SA	15	EtOH/RT	30	78	This work
12	SA	30	EtOH/RT	30	85	This work

Reaction conditions: Salicylaldehyde (1.0 mmol), o-phenylenediamine (1.0 mmol), [a] Isolated yield.; ,NC: Not completed

The workup procedure involves only filtration of synthesized product after adding cold water and washing with ethanol to give product. The synthesized products were confirmed by their spectral analysis such as ^{1}H, ^{13}C NMR, and MP. ^{1}H NMR ($CDCl_3$) spectrum of 3a exhibited two singlets around δ 13.09 ppm and d 8.66 ppm for −NH proton and -OH protons respectively, seven aromatic protons resonate as multiplets appeared at around d 6.92−7.42 ppm, $^{13}CNMR$ exhibited a signals around d 117, 118, 119, 119, 127, 132, 133, 142, 161, 163 ppm and in good correlation with literature data, confirms the predicted structure.

In order to verify scope and versatility of present transformation, we carried out reactions with different salicylaldehydes and notably found that salicylaldehydes containing both electron donating as well as electron withdrawing groups furnished desired 2(2'-hydroxy phenyl) benzimidazole in good yield (entry a- e; Table2) under optimized reaction conditions .

Table 2: Sulphamic acid catalyzed synthesis of substituted 2(2'-hydroxy phenyl) benzimidazole at ambient Temperature

Entry	Product 3	Time min	Yield (%)[a,b]	M.P obs (lit ^{O}C)[20]
a		30	92	240 (240-242)[20]
b		40	78	255
c		35	82	252
d		30	95	234
e		35	88	243

a All products exhibited satisfactory spectroscopic data. ^{1}H and ^{13}C NMR, ;[b] Yields refer to pure, isolated products

CONCLUSION

In conclusion, we have described an efficient synthesis of 2-(2-hydroxyphenyl) benzimidazole from two component condensation of salicylaldehyde, and o-phenylene diamine in ethanol medium at room temperature. Use of easily available sulphamic acid as catalyst, ethanol as nontoxic solvent systems and easy isolation of product are attractive features of the present transformation.

MATERIALS AND METHOD

General

All reagents were obtained from SIGMA ALDRICH and were used without further purification. Melting points were measured by open capillary. NMR spectra were recorded on a BrukerAC-300 MHz spectrometer in CDCl3 using tetramethylsilane as internal standard.

Method: Typical Procedure for synthesis of substituted 2-(2-hydroxyphenyl) benzimidazole.

A mixture of a salicylaldehyde (1 mmol), o-phenylene diamine (1 mmol) and 20 mol % of sulphamic acid in 5 mL ethanol was stirred at room temperature till completion of reaction for a period mentioned in Table 2. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was

poured into ice water, just filtered and washed with ethanol to furnish corresponding substituted- 2-(2-hydroxyphenyl)benzimidazole in high yields. These products were characterized by spectral techniques 1H, 13C NMR and MP.

ACKNOWLEDGEMENTS:

Authors MMM are thankful to Shivaji University Kolhapur for technical assistance.

SUPPORTING INFORMATION:

Data:

a 2-(2-Hydroxyphenyl)-1H-benzimidazole(3a) : m.p. 240 ^{0}C (ref [20] m.p. 242 ^{0}C; IR (KBr): 3325. 3043.47, 1604, 1530, 1489, 1279.88, 753.12; ^{1}H NMR (CDCl3, 300 MHZ, δ ppm): 6.92-6.97 (m, 1H), 7.06-7.08 (m, 2H), 7.24-7.29(m, 2H), 7.35-7.37(m, 2H),7.39-7.42 (m, 1H) 8.66(s, 1H, -OH), 13.09 (s, 1H, -NH); 13C NMR (CDCl3, 75 MHZ, d ppm)117.57, 118.99, 119.23, 119.75, 127.71, 132.34, 133.39, 142.58, 161.35, 163.74.

b. 2-(2'-Hydroxy-5'-ethoxy phenyl)-1H-benzimidazole(3b) : m.p. 255 ^{0}C; ^{1}H NMR (CDCl3, 300 MHZ, d ppm): 1.39-1.44 (t, 3H), 4.06-4.13 (q, 2H), 6.82-6.96 (m, 2H), 7.23-7.26 (m, 2H), 7.59-7.62(m, 3H), 13.08 (s, 1H, -NH); 13C NMR (CDCl3, 75 MHZ, d ppm) 14.84, 64.77, 111.12, 114.46, 115.64, 119.24, 119.55, 124.22, 134.22, 147.71, 148.09, 149.37.

c. 2-(2'-Hydroxy-5'-bromo phenyl)-1H-benzimidazole (3c) : m.p. 252 0C; 1H NMR (CDCl3, 300 MHZ, d ppm): 6.96-6.99 (d, 1H), 7.24-7.28 (m, 2H), 7.39-7.42(m, 1H), 7.44-7.45(d, 1H), 7.47-7.48(m, 1H), 7.52 (s, 1H), 8.58(s, 1H, -OH), 13.07 (s, 1H, -NH); 13C NMR (CDCl3, 75 MHZ, d ppm) 110.51, 119.58, 120.54, 121.74, 128.28, 134.28, 135.65, 139.73, 142.16, 160.34, 160.57, 162.36, 195.47.

d. 2-(2'-Hydroxy-3',5'-dichloro phenyl)-1H-benzimidazole(3d) : m.p. 234 ^{0}C; ^{1}H NMR (CDCl3, 300 MHZ, d ppm): 7.23-7.26 (m, 1H), 7.32-7.33 (m, 1H), 7.41-7.44 (m, 1H),7.49-7.50 (m, 1H),7.51-7.52 (m, 1H), 7.63-7.64(m,1H),8.58 (s, 1H, -OH), 13.63 (s, 1H, -NH).

e. 1-(1H-Benzoimidazol-2-yl)-naphthalen-2-ol(3e) : m.p. 243 ^{0}C; ^{1}H NMR (CDCl3, 300 MHZ, d ppm): 6.85-6.87 (t, 1H), 7.15-7.20 (m, 1H), 7.27-7.41 (m, 3H), 7.48-7.54 (t, 1H), 7.71-7.74 (d, 1H), 7.77-7.84 (m, 2H), 8.11-8.17(m, 1H), 9.45 (s, 1H, -OH), 15.08 (s, 1H, -NH); 13C NMR (CDCl3, 75 MHZ, d ppm) 118.62, 119.04, 119.21, 122.10, 124.53, 127.50, 128.11, 129.16, 129.40, 129.51, 133.37, 139.21, 148.46, 156.20, 193.34.

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Mansing M. Mane
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