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Benzimidazole Synthesis By Using Boron Sulfonic Acid As A New And Efficient Catalyst At Room Temperature

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Abstract: Boron sulfonic acid (BSA) was easily prepared and used as a new and efficient solid acid catalyst for the synthesis of benzimidazole derivatives with high isolated yields. Various substituted benzimidazoles were synthesized by a combination of o-phenylenediamines and aldehydes in the presence of boron sulfonic acid in with good yields in water and under a mild reaction conditions. This method is also applicable for precursors such as: aromatic and unsaturated aldehydes and *o*-phenylenediamines.
Keywords: Boron sulfonic acid, BSA, solid acid, benzimidazole synthesis, green synthesis.

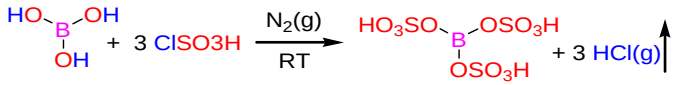
1. Introduction

Benzimidazole moieties are classified under several classes of drugs[1], based on the possible substitution at different positions of the benzimidazole nucleus. Benzimidazole derivatives exhibit significant activity against several viruses such as HIV, human cytomegalovirus (HCMV)[2], herpes (HSV-1)[3], RNA[4] and influenza[4,5]. Furthermore they have been also used to act as topoisomerase inhibitors[6], selective neuropeptide YY1 receptor antagonists[7], angiotensin II inhibitors[8], potential antitumor agents[9] and smooth muscle cell proliferation inhibitors[10]. In addition benzimidazoles are very important precursors in organic synthesis. Vitamin B_{12} constitutes a milestone in the chemistry of benzimidazoles. Bisbenzimidazole is DNA-minor grove binding agents possessing anti-tumour activity[11].

A number of methods have been reported for the synthesis of benzimidazoles such as the condensation of o-aryldiamines and aldehyde in refluxing nitrobenzene[12]. The coupling of phenylenediamines and carboxylic acids[13] or their derivatives (nitriles, imidates, or orthoesters)[14], which often requires strong acidic conditions[15], and sometimes combines with very high temperatures or microwave irradiation[16]. The other route involves a two-step procedure that includes the oxidative cyclo-dehydrogenation of Schiff bases, which are often generated from the condensation of *o*-phenylenediamines and aldehydes. Direct condensation of o-aryldiamines and aldehydes is not a good synthetic reaction, as it is well known to yield a complex mixture, being 1,2-disubstituted benzimidazoles, the bis anil and dihydrobenzimidazoles as the main side products[17]. However, the addition of transition metal, namely copper (II) acetate[18], mercury oxide[19] or lead tetracetate[20] allows a partial selective synthesis of benzimidazoles. In recent years, solvent-free synthesis of benzimidazoles under microwave irradiation using $Yb(OTf)_3$[21], KSF clay[22], PPA[23], Na_2SO_4[24], K-10 clay[25], metal halide supported alumina[26] and solid support[27] have been reported. Various oxidative and catalytic reagents such as sulfamic acid[28] , I_2[29], DDQ[30], Air[31], Oxone[32], $FeCl_3 \cdot 6H_2O$[33], $In(OTf)_3$[34], $Yb(OTf)_3$[35], $Sc(OTf)_3$[36], $KHSO_4$[37], IL[38], Nitrobenzene[39], 1,4-benzoquinone[40], tetracyano ethylene[41], benzofuroxan[42], MnO_2[43], $Pb(OAc)_4$[44], $NaHSO_3$[45], $Na_2S_2O_5$[46], DMP[47], NH_4VO_3[48], have been employed. Benzimidazole derivatives can be synthsised by another catalysts such as CAN[49], p-TsOH[50], $BE_3.OEt_2$[51], $KHSO_4$[52], $CuPy_2Cl_2$[53], polyphosphoric acid[54], mineral acids[55],

boric acid[56], p-TSA[57], Dowex 50W[58], SSA[59], solid acid scolecite[60], YCl_3[61], $Zn(OAc)_2$[62], *N*-halosuccinamide (X=Cl, Br, I)[63], $Yb(OTf)_3$[64], PEG-100[65], $(NH_4)H_2PW_{12}O_{40}$[66], bismuth chloride[67], mercury chloride[68], Ionic liquids[69], AMA[70], TBAF[71], H_2O_2/SiO_2-$FeCl_3$[72], HBF_4-SiO_2[73] and MoO_3/CeO_2-ZrO_2[74]. Unfortunately, many of these processes suffer some limitations, such as drastic reaction conditions, low yields, tedious work up procedures and co-occurrence of several side reactions. In this article, we report a simple and efficient method for the synthesis of benzimidazole derivatives using BSA[75-81] as a catalyst under mild reaction conditions. We used water as a green solvent. Water as a green reaction medium is highly appreciated. As a solvent, water possesses the following distinct advantages of being safe, nonflammable, readily available in large quantities, operationally very simple and devoid of any carcinogenic effects. Therefore, water mediated organic reactions for the preparation of biologically active molecules constitutes a major challenge for chemists involved in organic synthesis.

Firstly, BSA was introduced by Kiasat *et al* (**Scheme 1**) and used for the regioselective conversion of epoxides to thiocyanohydrins under solvent-free reaction conditions[82]. We converted it to BSA catalyst by using silica gel. We are investigating applications of this catalyst in organic synthesis.



Scheme 1. BSA synthesis

2. Experimental

2.1. General

IR spectra of the compounds were obtained on a Shimadzu IR-435 spectrometer using a KBr disk. The ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AQS 300 Avance instrument at 300 MHz in dimethyl sulfoxide (DMSO-d6) using tetramethylsilane as an internal standard. The progress of reaction was followed with thin-layer chromatography (TLC) using silica gel SILG/UV 254 and 365 plates. All the products are known compounds and were characterized by comparing the IR, ^1H NMR, and ^{13}C NMR spectroscopic data and their melting points with the literature values.

2.2. Typical procedure for the synthesis of benzimidazoles

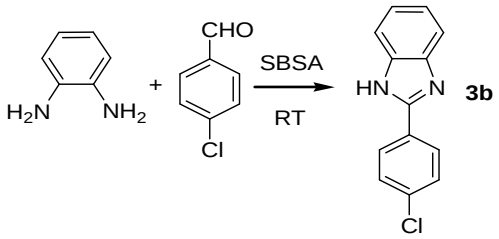
A mixture of o-phenylenediamine derivatives **1** (1 mmol), aromatic aldehyde **2** (1 mmol), and BSA/SiO_2 (0.05g, 5 mol %) in 10 mL of water, was stirred in a round bottomed flask at room temperature for 30 minutes (Table **2**). The progress of the reaction was followed by TLC. After completion of the reaction, the reaction mixture was added dropwise with vigorous stirring into a mixture of Na_2CO_3 (0.106g, 0.1 mmol) and H_2O (20 mL). In cases where the product precipitated as a free flowing solid, it was collected by filtration, washed with H_2O and dried. In cases where gummy material precipitated the product was extracted into EtOAc, the organic phace was washed with H_2O and dried with Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by column chromatography over silica gel (*n*-hexane:ethyl acetate, 5:1) to afford the corresponding benzimidazole. All of the compounds are known compounds which they were identified from their ^1H NMR spectroscopic data and by comparing their melting points with those reported in the literature[17-20,49,51,61-62,83-84].

2.3. Preparation of boron sulfonic acid (BSA)[75]

A 50 mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through water adsorbing solution and an alkali trap. Boric acid (1.55 g, 25 mmol) was charged in the flask and chlorosulfonic acid (8.74 g, ca. 5 mL, 75 mmol in 5 ml CH_2Cl_2) was added dropwise over a period of 1 h at room temperature under N_2(g). Hydrogen chloride evolved immediately. After completion of the addition, the mixture was shaken for 85 min, while the residual HCl was eliminated by suction. Then the mixture was washed with diethyl ether to remove the unreacted chlorosulfonic acid (^{1}HNMR of BSA in Acetone-D6 show δ=12.218) and then add 14.4 g silica gel and stirred those. Finally, dried and grayish solid material was obtained (21.6 g, 95.66%).

3. Results and Discussion

In continuation of our studies on sulfonic acid based catalysts such as silica sulforic acid (SSA), silica chloride, silica phosphoric acid, 1,3,5-Triazine-2,4,6-triyltrisulfamic acid (TTSA), ionic liquid with sulfonic acid moieties and so on, we decide to use boron sulfonic acid (BSA) for the synthesis of substituted benzimidazoles. Firstly, condensation of *o*-phenylenediamine and benzaldehyde was performed with different molar ratio of BSA, solvents and temperatures to optimize the reaction conditions. Various solvents with a good range of molar ratios of the catalyst were employed and the results are depicted in Table **1**. As shown in Table 1, a mixture of 5 mol% of BSA in H_2O (10 mL) created the best reaction media and afforded the benzimidazole **3b** with optimum yields among the conditions tested (entry 9, Table 1). In order to find a suitable catalyst ratio for the synthesis of benzimidazoles from 1,2-diamines and aldehydes, the condensation of benzene-1,2-diamine with 4-chlorobenzaldehyde was chosen as a model to provide compound **3b** (Scheme 2).

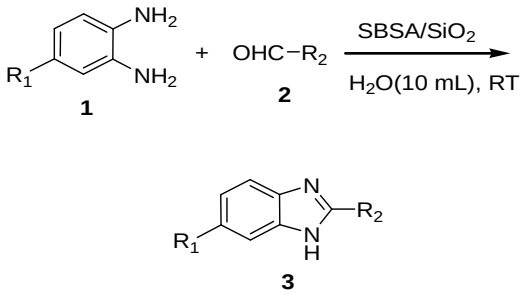


Scheme 2.

Table 1: Investigation of solvent effects and molar ratios of BSA for the synthesis of 2-(4-chlorophenyl)benzimidazole 3b at room temperature

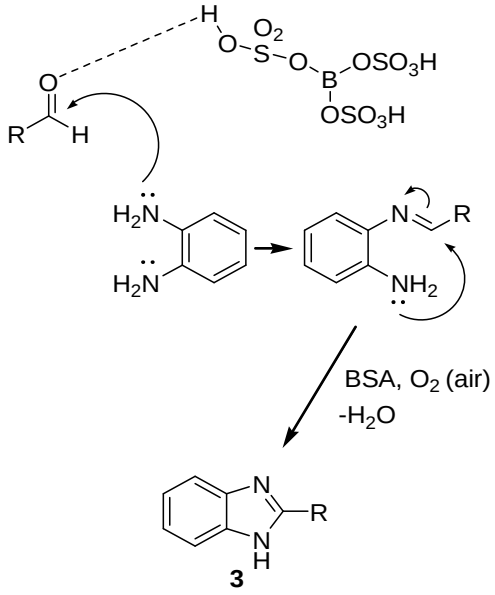
Entry	BSA%	Solvent	Time (min)	Yield%
1	5	CH_3CN	130	65
2	10	CH_3COOEt	100	78
3	5	CH_3COOEt	120	77
4	10	EtOH	80	80
5	5	EtOH	90	73
6	20	H_2O	35	90
7	15	H_2O	35	90
8	10	H_2O	35	90
9	5	H_2O	25	97
10	3	H_2O	45	93
11	5	*n*-Hexane	150	45

Herein, we wish to report a novel protocol for the rapid synthesis of a variety of biologically significant benzimidazoles using a catalytic amount of BSA under mild aqueous conditions (Scheme 3). The reaction was carried out in neat at room temperature for 30 minutes, using o-phenylenediamine (1 mmol) and aldehyde (1 mmol) in the presence of BSA (0.05 mmol). The results are summarized in Table 2.



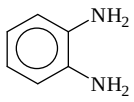
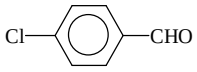
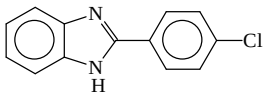
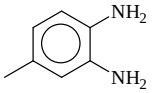
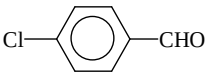
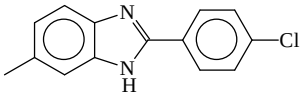
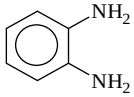
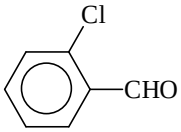
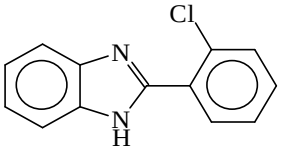
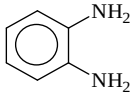
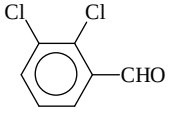
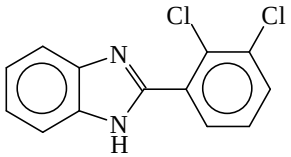
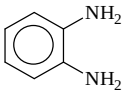
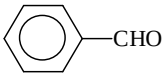
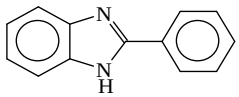
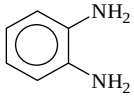
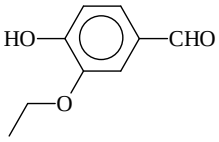
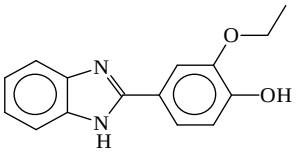
Scheme 3. Synthesis of 1,3-benzimidazole derivatives 3 from the reaction of *o*-phenylenediamines with various aldehydes.

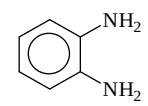
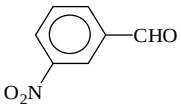
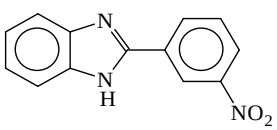
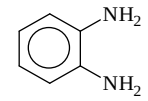
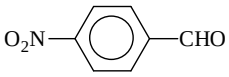
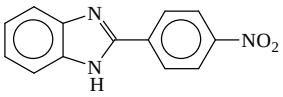
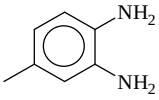
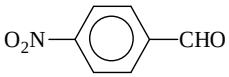
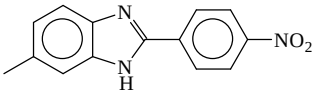
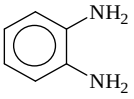
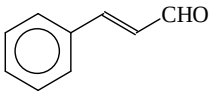
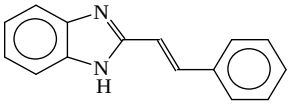
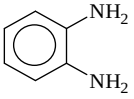
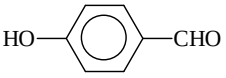
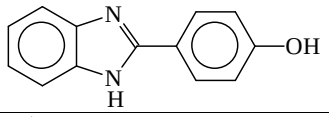
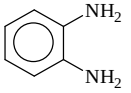
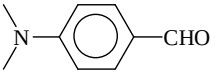
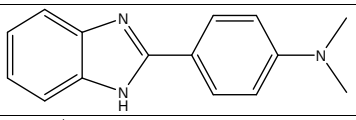
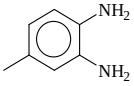
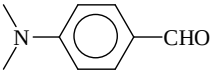
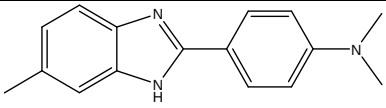
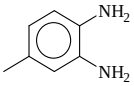
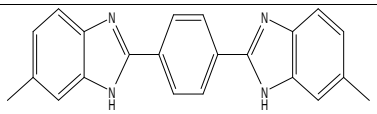
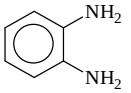
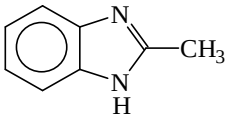
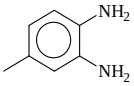
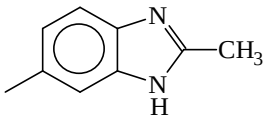
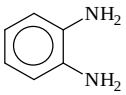
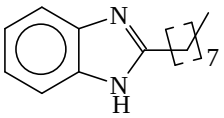
The reasonable mechanism as shown below (**Scheme 4**).



Scheme 4. Mechanisms for the synthesis of 1- and 2-substitute-1,3-benzimidazoles 3 via condensation reaction of phenylenediamines with different aldehydes

Table 2. Synthesis of benzimidazoles catalyzed by BSA

Entry	Diamine 1	Aldehyde 2	Product 3	Yield%[a] [ref.]
a				97 [51, 61, 76]
b				98
c				93 [76]
d				91
e				93 [49, 51, 61, 71]
f				82 [51]

g				93 [51, 62, 71]
h				96 [62, 77]
i				98 [62]
j				97 [61]
k				84 [51, 61]
l				78 [62]
m				81 [62]
n				83
o		CH_3CHO		Trace
p		CH_3CHO		trace
q		hexanal		trace

[a]Isolated yields.

4. Conclusions

In conclusion, we have developed a one-pot, simple and efficient method for the synthesis of 2-arylsubstituted benzimidazoles by the condensation of o-phenylenediamine with arylaldehyde catalyzed by BSA. As shown in Table 2, a wide variety of aromatic compounds and α,β-unsaturated aldehydes having both electron- donating and electrone withdrawing groups and substituted o-phenylenediamine react to give the corresponding benzimidazole in good yields. Best results were obtained using 0.15 equivalents of BSA, lower loading resulted in lower yields, while higher loading did not increase product yields significantly. This method offers several advantages such as high conversions, shorter reaction times, non-toxic cost efficiency providing, recyclability of the catalyst, cleaner reaction profiles and simple experimental and work-up procedures. In summary, a simple work-up procedure, mild reaction conditions and very good yields make our methodology a valid contribution to the existing processes in synthesis of benzimidazole derivatives. The aliphatic aldehydes which also were not reacted under similar conditions gave considerable yields (Table 2, entries **3o-q**).

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