J IRAN CHEM SOC
DOI 10.1007/s13738-015-0592-1

ORIGINAL PAPER

Synthesis of 2-substituted benzimidazoles and benzothiazoles using Ag_2CO_3/Celite as an efficient solid catalyst

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Received: 9 October 2014 / Accepted: 2 January 2015

Abstract An efficient and simple approach for the synthesis of 2-substituted benzimidazoles and benzothiazoles through a coupling of 1,2-phenylenediamines and 2-aminothiophenols with variety of aryl aldehydes in ethanol at 70 °C using Ag_2CO_3/Celite as solid catalyst is described. The procedure features short reaction time, excellent yields and simple workup.

Keywords Benzimidazole · Benzothiazole · 1,2-Phenylenediamine · 2-Aminothiophenol · Ag_2CO_3/Celite

The benzimidazoles and benzothiazoles are important class of heterocyclic compounds that exhibit a wide range of biological properties such as antiviral, antiulcer, antihypertension, antifungal, antihistaminic, and anticancer [1–11]. These compounds are also good versatile intermediate for synthesis of many important organic compounds [12, 13].

The most common approach for the synthesis of 2-substituted benzimidazoles and benzothiazoles involves the treatment of 1,2-phenylenediamines and 2-aminothiophenol with carboxylic acids [14–18] or their derivatives [19–21], under strongly acidic conditions with very high temperatures or the use of microwave irradiation [22–24]. Another approach for the synthesis of these compounds is including condensation of 1,2-phenylenediamines and 2-aminothiophenol with aldehydes [25–33] under oxidative conditions using various oxidative and catalytic reagents [25–54] such as such as nitrobenzene [25], 1,4-benzoquinone [26], $PhI(OAc)_2$ [27], Zn-proline [28], (DDQ) [29], MnO_2 [30], $Pb(OAc)_4$ [31], oxone [32], $NaHSO_3$ [33], H_2O_2/HCl [34], CAN [35], iodine [36], $FeCl_3{\cdot}6H_2O$ [37], $In(OTf)_3$ [38], $Yb(OTf)_3$ [39], $Sc(OTf)_3$ [40], $Cu(OTf)_2$ [41], $KHSO_4$ [42], $ZrOCl_2{\cdot}8H_2O$ [43], $ZrCl_4$ [44], $HfCl_4$ [44], boron trifluoride etherate [45], cobalt complexes [46], cerium complexes [35].

Although the reactions were efficiently promoted by the above-mentioned conditions, they often employed homogeneous catalysts and also some of those methods suffer from one or more disadvantages, such as usage of stoichiometric reagent, prolonged reaction times and difficulty in separation of the products and recovery of the catalyst from the reaction mixture. Therefore, the discovery of mild and practicable, stable, cheap, recyclable, and ecofriendly heterogeneous catalysts for the synthesis of 2-substituted benzimidazoles and benzothiazoles are still in serious demand that can attract the attention of researchers.

Ag_2CO_3/Celite (Fetizon's reagent) [55], a very mild oxidant and easily available oxidizing agent, has been widely used in organic reactions [56–63]. Moreover, this reagent was extensively used for oxidation of alcohols. But the catalytic application of this reagent has not been carefully studied in the synthesis of 2-substituted benzimidazoles and benzothiazoles until now. During our research in organic synthesis, we have found that Ag_2CO_3/Celite could effectively catalyze the synthesis of 2-substituted benzimidazoles and benzothiazoles.

Due to the aforementioned reasons, and as a part of our ongoing research to develop new synthetic methodologies

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Published online: 18 January 2015

Scheme 1 Synthesis of 2-substituted benzimidazoles and benzothiazoles

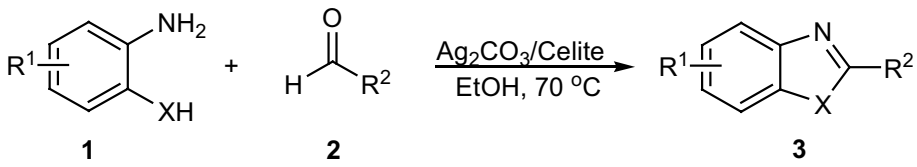
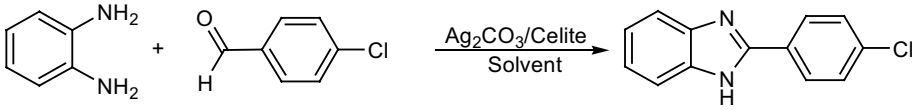


Table 1 Optimization of the reaction

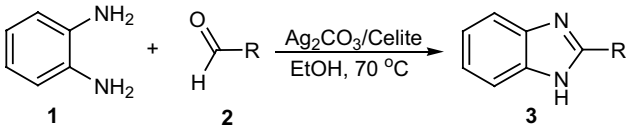


Entry	Solvent	Time (h)	Catalyst (mol %)	Temperature (°C)	Yield (%)
1	EtOH	3	Ag_2CO_3/Celite (25 mol %)	70	96
2	H_2O	3	Ag_2CO_3/Celite (25 mol %)	70	65
3	CH_3CN	3	Ag_2CO_3/Celite (25 mol %)	70	0
4	EtOAc	3	Ag_2CO_3/Celite (25 mol %)	70	0
5	Toluene	3	Ag_2CO_3/Celite (25 mol %)	70	0
6	CH_2Cl_2	3	Ag_2CO_3/Celite (25 mol %)	25	0
7	EtOH/H_2O (2:1)	3	Ag_2CO_3/Celite (25 mol %)	70	81
8	EtOH/H_2O (1:1)	3	Ag_2CO_3/Celite (25 mol %)	70	76
9	EtOH/H_2O (1:2)	3	Ag_2CO_3/Celite (25 mol %)	70	71
10	EtOH	12	Ag_2CO_3/Celite (25 mol %)	25	0
11	EtOH	3	Ag_2CO_3/Celite (25 mol %)	50	60
12	EtOH	3	Ag_2CO_3/Celite (25 mol %)	100	96
13	EtOH	3	Ag_2CO_3/Celite (5 mol %)	70	35
14	EtOH	3	Ag_2CO_3/Celite (10 mol %)	70	50
15	EtOH	3	Ag_2CO_3/Celite (15 mol %)	70	65
16	EtOH	3	Ag_2CO_3/Celite (20 mol %)	70	86
17	EtOH	3	Ag_2CO_3/Celite (30 mol %)	70	96
18	EtOH	12	Without catalyst	70	0

[64–67], we report herein simple and efficient in situ tandem cyclocondensation–oxidation sequence reaction of 1,2-phenylenediamine and 2-aminothiophenol with various alkyl and aryl aldehydes for the preparation of 2-substituted benzimidazoles and benzothiazoles in ethanol at 70 °C using Ag_2CO_3/Celite as solid catalyst in excellent yield (Scheme 1).

We chose the reaction of 1,2-phenylenediamine with 4-chlorobenzaldehyde as a model system for the optimization study (Table 1). First, we compared the reaction rate in different solvents by measuring the isolated yield using identical amounts of reactants and catalyst (25 mol % of Ag_2CO_3/Celite) for a fixed reaction time of 3 h at 70 °C (Table 1, entries 1–6). The desired products were scarcely obtained in aprotic solvents such as ethyl acetate, toluene, acetonitrile, and dichloromethane (Table 1, entries 3–6). But when the reaction was carried out using the protic solvents such as ethanol, water and water/ethanol mixture (Table 1, entries 1–2, 7–9), the results indicated that although water and water/ethanol mixture were found to be effective for this reaction system, the best result was obtained when ethanol was utilized as solvent. This effect can be explained by a simple acid-catalysis mechanism facilitated by the strong hydrogen bond interaction at the organic–water or ethanol interface which stabilizes the reaction intermediate. Next, we studied the model reaction in ethanol at different temperatures (Table 1, entry 1 and entries 10–12). The reaction rate increased as the temperature was raised. At 70 °C, the maximum yield (96 %) was obtained in a reaction time of 3 h (Table 1, entry 1). Also, the model reaction was studied in ethanol at 70 °C using different amounts of Ag_2CO_3/Celite (Table 1, entry 1 and entries 13–17). The best results were obtained with 25 mol % of Ag_2CO_3/Celite (Table 1, entry 1). Further work indicated that the best results are obtained when the reaction is performed at 70 °C for 3 h using Ag_2CO_3/Celite (25 % mol) in ethanol.

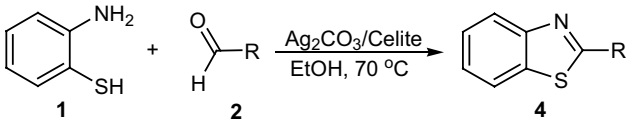
Table 2 Synthesis of benzimidazole derivatives by using 1,2-phenylenediamines and aromatic aldehydes



1 2 3

Entry	R	X	Product	Yield (%)	Mp (°C)	
					Found	Reported
1	Ph	H	**3a**	**95**	**292**	290–291 [68]
2	4-$CH_3C_6H_4$	H	**3b**	**91**	**269**	270 [69]
3	4-FC_6H_4	H	**3c**	**96**	**246–247**	247–248 [70]
4	4-OHC_6H_4	H	**3d**	**94**	**279**	279 [71]
5	4-$N(CH_3)_2C_6H_4$	H	**3e**	**92**	**229–230**	228–229 [72]
6	4-ClC_6H_4	H	**3f**	**96**	**300–302**	301 [73]
7	4-$O_2NC_6H_4$	H	**3g**	**97**	**>300**	324–326 [78]
8	4-BrC_6H_4	H	**3h**	**97**	**293–295**	295–296 [79]
9	4-$HCOC_6H_4$	H	**3i**	**95**	**>300**	>300
10	3-$O_2NC_6H_4$	H	**3j**	**95**	**205–206**	207–208 [75]
11	2-$CH_3OC_6H_4$	H	**3k**	**90**	**225–226**	[227–228] [7–11]
12	2-Pyridyl	H	**3l**	**99**	**220–223**	218 [69]
13	2-OHC_6H_4	H	**3m**	**95**	**241–242**	[242] [14–18]
14	2-Furyl	H	**3n**	**88**	**286–288**	288 [69]
15	C_6H_5-CH=CH	H	**3o**	**91**	**200–202**	201–203 [74]
16	Ph	CH_3	**3p**	**94**	**238–240**	240–241 [76]
17	4-$CH_3C_6H_4$	CH_3	**3q**	**91**	**189–191**	190–191 [77]

Table 3 Synthesis of benzothiazole derivatives by using 1,2-benzothiazoles and aromatic aldehydes



1 2 4

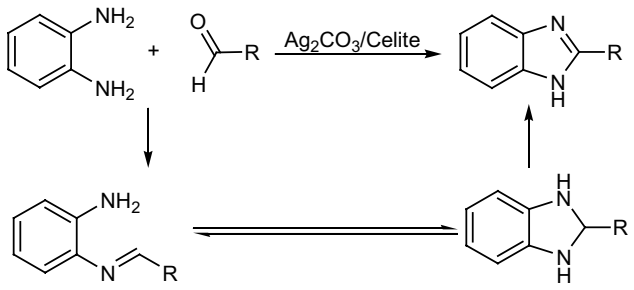
Entry	R	Product	Yield (%)	Mp (°C)	
				Found	Reported
1	Ph	**4a**	**93**	**114**	113–114 [22]
2	4-$CH_3C_6H_4$	**4b**	**90**	**86**	85 [80]
3	4-$N(CH_3)_2C_6H_4$	**4c**	**93**	**170–172**	170–171 [71]
4	4-OHC_6H_4	**4d**	**94**	**231–232**	231–232 [81]
5	4-FC_6H_4	**4e**	**95**	**100**	98–99 [82]
6	4-ClC_6H_4	**4f**	**96**	**117–119**	119–120 [82]
7	4-$O_2NC_6H_4$	**4g**	**97**	**226–227**	225–226 [80]
8	4-NCC_6H_4	**4h**	**95**	**170**	170 [85]
9	4-$CH_3COC_6H_4$	**4i**	**96**	**179**	178–180 [83]
10	2-Furyl	**4j**	**90**	**105**	103–104 [84]
11	2-OHC_6H_4	**4k**	**94**	**121**	[122] [86]
12	2-Pyridyl	**4l**	**98**	**135**	129–130 [71]
13	2-OH-4-BrC_6H_4	**3m**	**95**	**169–169.5**	[170] [19–21]
14	C_6H_5-CH=CH	**3n**	**93**	**109–111**	110–111 [84]

To illustrate the need for Ag_2CO_3/Celite, the feasibility of model reaction is checked in the absence of Ag_2CO_3/Celite. No product was obtained at 70 °C even after 12 h. Therefore, Ag_2CO_3/Celite is obviously an important component of the reaction.

With the optimized condition established above, our next attempt was to extend the capability of this process to two 1,2-phenylenediamines such as 1,2-phenylenediamine and 4-methyl-1,2-phenylenediamine and various types of aryl aldehydes. The results are summarized in Table 2. In all cases, excellent yields were obtained, even in the presence of electron-donating or electron-withdrawing substituents on the aldehydes. This result confirms the reliability of the present synthetic methodologies. Notably, this protocol has also its limitations. Aliphatic aldehydes only provided very low yields of the desired products or did not offer any desired product.

To expand the synthetic scope of this protocol, we carried out the reaction using 2-aminothiphenol instead of o-phenylenediamine. The reaction worked well using various substituted aldehydes furnishing the corresponding benzimidazoles in excellent yields (Table 3).

As per a plausible mechanism, the reaction proceeds via the activation of aldehyde by Ag_2CO_3/Celite followed



Scheme 2 Proposed mechanism

by imine formation. The resulting imine further reacts with another NH_2 group of 1,2-phenylenediamine resulting in the formation of dihydroimidazole which subsequently undergoes aromatization under the oxidative conditions (Ag_2CO_3) to give the benzimidazole as shown in Scheme 2.

In conclusion, we have introduced the utilization of Ag_2CO_3/Celite, as a heterogeneous catalyst, for simple and efficient synthesis of 2-substituted benzimidazoles and benzothiazoles through the condensation of 1,2-phenylenediamines and 2-aminothiophenols with various aryl aldehydes. This method offers some advantages in terms of simplicity of performance, short reaction times, excellent yields, and mild condition. The current protocol could also serves as a valuable alternative to known reaction systems.

Experimental

General procedure for the synthesis of 2-substituted benzimidazoles and benzothiazoles

To a mixture of 1,2-phenylenediamines (1.0 mmol) and aldehydes (1.1 mmol) in ethanol, 25 mol % of Ag_2CO_3/Celite (3 mL) was added. The resulting mixture was stirred at 70 °C for 3 h. After this time, the reaction mixture was diluted with ethanol (50 mL) and the catalyst was separated by filtration. Water was then added to the organic layer, and the products were filtered and washed with water. All of the products are known compounds and characterized easily by comparison with melting point, IR, [1–6] H NMR spectral data reported in literature.

Acknowledgments We gratefully acknowledge financial support from the Iran National Science Foundation (INSF) and Research Council of Razi University.

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