Synthesis of 1,2-disubstituted benzimidazoles, 2-substituted benzimidazoles and 2-substituted benzothiazoles in SDS micelles†

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A practical and convenient synthetic method has been developed for the facile synthesis of 1,2-disubstituted benzimidazoles, 2-substituted benzimidazoles and 2-substituted benzothiazoles. The method described has the benefits of operational simplicity, excellent yields, and high chemoselectivity.

Introduction

Benzimidazole derivatives have versatile pharmacological properties[1] based on their presence in both clinical medicines[2] and compounds with broad ranges of biological functions.[3] Also, compounds with benzothiazole skeletons are of paramount interest because of their antitumor,[4] anticancer,[5] and antibacterial[6] activities. Thus synthesis of this heterocyclic nucleus is therefore of continuing interest, but few methods are available for the synthesis of 1,2-disubstituted benzimidazoles. The more important ones include: *N*-alkylation of 2-substituted benzimidazole in the presence of a strong base,[7] *N*-alkylation of *o*-nitroanilides followed by reductive cyclization,[8] cyclocondensation of *N*-substituted *o*-aminoanilides,[9] and condensation of *N*-substituted phenylenediamines with the sodium salt of α-hydroxybenzylsulfonic acid.[10] In addition, 1,2-disubstituted benzimidazoles can also be accessed by direct one-step condensation of 1,2-phenylenediamines with aryl aldehydes under the influence of a variety of acid catalysts.[11] However, the last protocol is currently most popular, probably because of the ease of accessibility of substituted aryl aldehydes.

Two protocols are usually followed for the synthesis of 2-substituted benzimidazoles. The first is the coupling of 1,2-phenylenediamines with carboxylic acids or their derivatives,[12] and the second route involves condensation of 1,2-phenylenediamine and aldehydes followed by oxidative cyclodehydrogenation.[13]

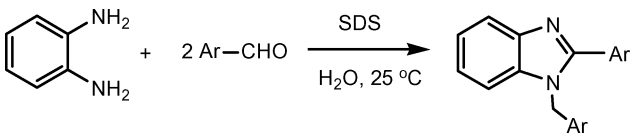
Many methods are available for the preparation of 2-substituted benzothiazoles,[14] but the most popular approaches generally involve condensation–dehydration of 2-aminothiophenol with carboxylic acids,[15] or condensation with aldehydes under oxidative conditions.[16]

Although these methods are quite satisfactory, many of them employ considerable amounts of hazardous organic solvents; in addition, several require higher temperatures and costly reagents. Moreover, one of the major limitations of these methodologies is that they show poor selectivity in terms of N-1 substitution, which results in the formation of two compounds (*i.e.*, the formation of 2-substituted benzimidazole along with 1,2-disubstituted benzimidazole as a mixture).

Developing environmentally benign and economical syntheses is an area of research that is being vigorously pursued, and avoiding the use of harmful organic solvents is a fundamental strategy to achieving this. One of the most attractive alternatives to organic solvents is water, which has witnessed increasing popularity due to being inexpensive, readily available and environmentally benign. In addition, reactions in aqueous media illustrate unique reactivities and selectivities that are not usually observed in organic media.[17] However, organic reactions in water are often limited in scope due to poor solubility of the organic compounds. A possible new way to improve the solubility of substrates is the use of surface-active compounds that can form micelles.[18]

Under ambient conditions, surfactant molecules can aggregate in an aqueous phase to form micelles with a hydrophobic core and a hydrophilic corona. The use of micellar surfactants as catalysts is widespread, and has been investigated in detail for various reactions in aqueous solutions.[19]

As a part of our continued activities in this area,[20] we report for the first time a simple and efficient method for the synthesis of 1,2-disubstituted benzimidazoles through the reactions of 1,2-phenylenediamine with aryl aldehydes in aqueous micellar media, using sodium dodecylsulfate (SDS), which simultaneously functions as a catalyst to promote the reactions and as a surfactant to assist in solubilizing the organic substrates (Scheme 1). SDS was chosen since it forms micelles in water, can solubilize organic compounds, and has been used successfully in a number of organic reactions as a catalyst.[21]



Scheme 1 Selective synthesis of 1,2-disubstituted benzimidazoles.

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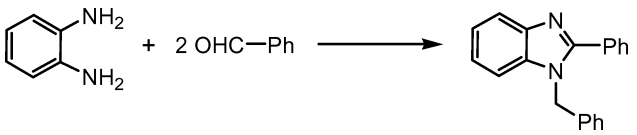
Table 1 Optimization of the reaction conditions[a]



Entry	SDS (mol%)	Yield (%)[b]
1	0	23[c]
2	5	40
3	7	70
4	10	98
5	15	98

[a] Reaction conditions: The reactions were performed with 1,2-phenylenediamine (1 mmol) and benzaldehyde (2 mmol) in the presence of different amount of SDS as catalyst for 22 min, at 25 °C in H_2O (5 mL) as solvent. [b] Isolated yields. [c] Reaction not complete after 5 h.

Results and discussion

We started this synthesis by examining the reaction of 1,2-phenylenediamine (1 mmol) with benzaldehyde (2 mmol) as a model reaction. As shown in Table 1, the use of SDS allowed the direct conversion of 1,2-phenylenediamine into the corresponding 1,2-disubstituted benzimidazole in a yield of 98% in water (5 mL) at 25 °C (Table 1, entry 4). The use of more than 10 mol% of SDS did not enhance chemical yield (Table 1, entry 5).

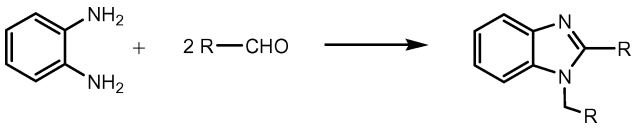
It is noteworthy that in a control experiment (Table 1, entry 1), no significant promotion was observed under similar reaction conditions in the absence of SDS, and only a low yield was obtained after 5 h. SDS is an emulsifying agent, which catalyzes this reaction and forms stable colloidal particles in the presence of the substrates in water, and this colloid formation plays an important role in acceleration of the reactions.[21e]

To test the generality of this reaction, a series of aromatic aldehydes was subjected to the optimal reaction conditions (Table 2). By using water as solvent at 25 °C, 1,2-disubstituted benzimidazoles with various functional groups were obtained in excellent yields. Among the reactions of different aromatic aldehydes, no significant distinction on the yields of target products was observed. Even the sensitive substrate furfuraldehyde (Table 2, entry 10) produced the corresponding 1,2-disubstituted benzimidazole without any difficulty. All substrates gave their corresponding 1,2-disubstituted benzimidazoles exclusively as a single product. However, butyraldehyde failed to react under the present reaction conditions.

A possible mechanism for the reaction consists of a two-step sequence involving the micelle-promoted formation of the *N*,*N*-dibenzylidene-1,2-phenylenediamine derivative followed by ring closure. Aromatization then takes place by a deprotonation–reprotonation process.[22]

The catalytic effect of micellar sodium dodecyl sulfate in this reaction can be explained as follows. In the micellar solution, 1,2-phenylenediamine and aryl aldehyde, which are both hydrophobic, are forced inside the hydrophobic core of the micelles, thus allowing the reaction to take place more easily (Fig. 1).

Table 2 Synthesis of 1,2-disubstituted benzimidazoles in SDS micellar solution[a]



Entry	R	Time/min	Yield (%)[b]	Mp/°C (lit.)	Ref.
1	C_6H_5	22	98	132 (132)	11*d*
2	4-$MeOC_6H_4$	25	97	127 (129–130)	11*d*
3	4-HOC_6H_4	10	94	226 (222)	23
4	4-MeC_6H_4	27	93	126–128 (128–130)	11*i*
5	4-$(Me_2N)C_6H_4$	20	75	253 (255)	11*i*
6	2-ClC_6H_4	10	93	163 (158–159)	24
7	4-ClC_6H_4	22	95	134 (136)	11*g*
8	4-NO_2-C_6H_5	30	90	304 (306–308)	25
9	2-Pyridyl	8	98	125 (130)	11*g*
10	2-Furyl	23	95	96 (94)	11*d*
11	$CH_3(CH_2)_2$	120	0	—	—

[a] The products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by reported procedures. [b] Yields refer to pure isolated products.

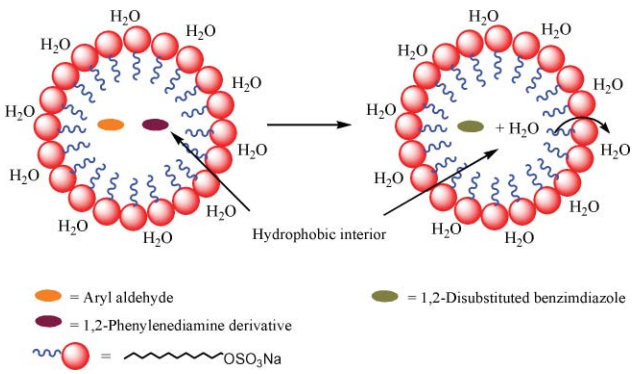


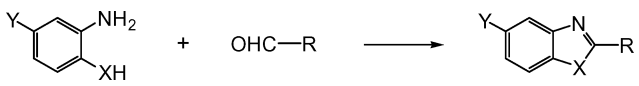
Fig. 1 Proposed model for the synthesis of 1,2-disubstituted benzimidazole in water in the presence of SDS.

The scope of this system has been successfully extended to the synthesis of 2-substituted benzimidazoles, which represents the first synthesis of these compounds in water through such transformations (Scheme 2). The optimum conditions were 1,2-phenylenediamine (1 mmol) and aldehyde (1 mmol), in the presence of $(NH_4)_2S_2O_8$ (1 mmol) and SDS (10 mol%) in water at 25 °C (Fig. 2).

Fig. 2 Photographs of the reaction of 1,2-phenylenediamine with benzaldehyde in the presence of $(NH_4)_2S_2O_8$ and SDS H_2O at 25 °C: (a) at the start of the reaction; (b) in the middle of the reaction; and (c) at the end of the reaction.

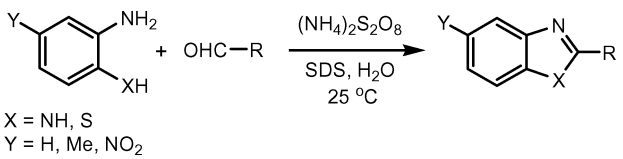
Aromatic aldehydes with electron-donating and electron-withdrawing groups both participated in this reaction equally

Table 3 Synthesis of 2-substituted benzimidazoles and 2-substituted benzothiazoles in SDS micellar solution[a]



Entry	R	Y	X	Time/min	Yield (%)[b]	Mp/°C (lit.)	Ref.
1	C_6H_5	H	NH	22	97	293 (295)	28*a*
2	4-$MeOC_6H_4$	H	NH	25	97	223–226 (226)	13*a*
3	4-MeC_6H_4	H	NH	27	93	271 (270)	13*a*
4	4-$(Me_2N)C_6H_4$	H	NH	20	95	232 (228–229)	28*b*
5	4-HOC_6H_4	H	NH	10	94	275 (279)	28*c*
6	4-FC_6H_4	H	NH	28	96	248 (247–248)	28*d*
7	4-ClC_6H_4	H	NH	22	95	300 (301)	28*e*
8	3-NO_2-C_6H_4	H	NH	20	94	203 (207–208)	28*f*
9	C_6H_5CH=CH	H	NH	40	90	200 (201–203)	13*d*
10	2-Furyl	H	NH	23	95	286 (288)	13*a*
11	2-Pyridyl	H	NH	10	99	222–224 (218)	13*a*
12	C_6H_5	Me	NH	18	98	236 (240–241)	28*g*
13	4-MeC_6H_4	Me	NH	24	96	195 (190–191)	28*h*
14	4-$MeOC_6H_4$	Me	NH	20	94	171 (169)	28*i*
15	4-FC_6H_4	Me	NH	25	97	180 (180–183)	20*b*
16	C_6H_5	NO_2	NH	32	94	203 (207–208)	28*h*
17	4-ClC_6H_4	NO_2	NH	35	95	302 (305–308)	28*h*
18	CH_3	H	NH	120	15	173–175 (177–178)	12*b*
19	$CH_3(CH_2)_2$	H	NH	120	12	147–148 (148–149)	28*l*
20	$CH_3(CH_2)_4$	H	NH	120	Trace	—	—
21	C_6H_5	H	S	20	95	114 (113–114)	28*d*
22	4-$MeOC_6H_4$	H	S	20	95	121 (119–120)	28*d*
23	4-MeC_6H_4	H	S	24	96	85–86 (85)	28*j*
24	4-$(Me_2N)C_6H_4$	H	S	20	97	173 (170–171)	28*b*
25	4-HOC_6H_4	H	S	22	96	231 (231–232)	28*k*
26	4-FC_6H_4	H	S	24	94	98–100 (98–99)	28*m*
27	4-ClC_6H_4	H	S	24	95	114 (119–120)	28*m*
28	C_6H_5CH=CH	H	S	15	98	113 (110–111)	15*c*
29	4-NO_2-C_6H_4	H	S	16	95	228 (225–226)	28*d*
30	CHO-C_6H_4	H	S	28	96	132 (135–136)	20*b*
31	2-Pyridyl	H	S	10	99	134 (129–130)	28*b*
32	2-Furyl	H	S	20	95	106 (103–104.5)	15*c*

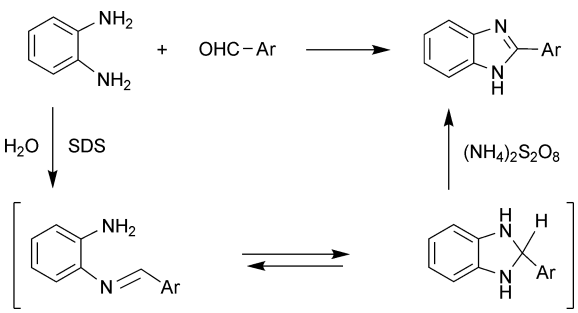
[a] The products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by reported procedures.
[b] Yields refer to pure isolated products.



Scheme 2 Selective synthesis of 2-substituted benzimidazole and 2-substituted benzothiazoles.

well – apparently, the nature and position of substitution on the aryl ring does not make much difference in reactivity. Similarly, heterocyclic aldehydes and those containing an α,β-unsaturated group afforded excellent yields of the products, without formation of any side-products. This condensation–oxidation procedure is fairly general, and several functionalities, including hydroxyl and conjugated carbon–carbon double bonds, are tolerated (Table 3).

For the oxidation of cyclic intermediates, we selected ammonium persulfate, $(NH_4)_2S_2O_8$, because it is a very strong oxidant, very soluble in water, nonhazardous and relatively cheap.[26] In this case, acts both as a peroxide booster (providing additional nascent oxygen to the aqueous solution) and as a mild oxidizing agent[27] (Scheme 3).



Scheme 3 A possible pathway for synthesis of 2-aryl benzimidazoles.

Nevertheless, this protocol has its limitations. Aliphatic aldehydes such as acetaldehyde, butylaldehyde and hexylaldehyde show extremely poor yields of the desired products (Table 3, entries 18–20).

Employing the same procedure given above but using 2-aminothiophenol instead of 1,2-phenylenediamine, the corresponding 2-aryl benzothiazole derivatives were obtained in excellent yields with various substituents (Scheme 2; Table 3, entries 21–32). The limitations on the use of the aldehydes were similar to those for 1,2-phenylenediamines.

Conclusion

In summary, a practical and convenient synthetic method in aqueous media using SDS as the surfactant catalyst (10 mol%) has been developed for the facile synthesis of 1,2-disubstituted benzimidazoles, 2-substituted benzimidazoles and 2-substituted benzothiazoles. The operational simplicity, excellent yields of the products, and high chemoselectivity are the main advantages of this method, and furthermore, this procedure is cheap, safe and environmentally benign.

Experimental

General

Sodium dodecyl sulfate, ammonium persulfate, 1,2-phenylenediamine derivatives, 2-aminothiophenol, and the aldehyde substrates were purchased from the Merck Chemical Company, and were used without further purification. Melting points were determined in a capillary tube and are not corrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-200 NMR spectrometer using TMS as internal standard.

General procedure for the synthesis of 1,2-disubstituted benzimidazoles

The aryl aldehyde (2 mmol) and 1,2-phenylenediamine (1 mmol) were added to a solution of SDS (10 mol%, 0.03 g) in H_2O (5 mL), and the mixture stirred at room temperature for the time given (Table 2). The progress of the reaction was monitored by TLC (eluent: 7:3 *n*-hexane–ethyl acetate). After completion of the reaction, K_2CO_3 (0.5 mmol, 0.07 g) was added to the reaction mixture, and the resulting precipitate of dodecyl sulfate filtered off. The filtrate was extracted with ethyl acetate (4 × 10 mL), dried over anhydrous $MgSO_4$ and evaporated to give analytically pure product. When necessary, the crude product was recrystallized from EtOH.

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

The 1,2-phenylenediamine derivative (1 mmol), aryl aldehyde (1 mmol), and $(NH_4)_2S_2O_8$ (1 mmol, 0.23 g) were added to a solution of SDS (10 mol%, 0.03 g) in H_2O (5 mL), and the mixture stirred at room temperature until the starting materials were consumed (see Table 3). The progress of the reaction was monitored by TLC (eluent: 7:3 *n*-hexane–ethyl acetate). After completion of the reaction, K_2CO_3 (0.5 mmol, 0.07 g) was added to the reaction mixture, and the resulting precipitate of dodecyl sulfate filtered off. The filtrate was extracted with ethyl acetate (4 × 10 mL), and dried over anhydrous $MgSO_4$, and evaporated to give the benzimidazole. An identical procedure was employed using 2-aminothiophenol (1 mmol) and aryl aldehyde (1 mmol) in the presence of $(NH_4)_2S_2O_8$ (1 mmol) for the synthesis of benzothiazoles (Table 2).

All of the products are known compounds, and their identity was easily confirmed by comparison with authentic samples (^{1}H NMR, ^{13}C NMR, mp).

Acknowledgements

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