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ORIGINAL PAPER

Sulfamic acid as a recyclable and green catalyst for rapid and highly efficient synthesis of 2-arylbenzothiazoles in water at room temperature

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Abstract 2-Arylbenzothiazoles have been synthesized in water in good to excellent yield from direct condensation of various aromatic aldehydes with 2-aminothiophenol promoted by catalytic amount of sulfamic acid at room temperature. This method provides a simple, rapid and efficient protocol in terms of mild reaction conditions, clean reaction profiles, small quantity of catalyst and simple work-up procedure.

Keywords Condensation reaction · Sulfamic acid · Catalyst · 2-Arylbenzothiazoles

Introduction

The exploration of privileged structures in drug discovery is rapidly emerging theme in medicinal chemistry. Benzothiazole and its derivatives belong to such immensely important class of heterocyclic systems, owing to their potent antitumor activity [1] and other important pharmaceutical utilities [2]. Also, they have been widely used in industry as antioxidants and vulcanization accelerators that highlight their synthetic necessity [3]. Numerous methods have been reported in the literature for the synthesis of benzothiazoles. The most popular approaches generally involve: (1) condensation of 2-aminothiophenols with carboxylic acids and their derivatives [4–6] or condensation with aldehydes under oxidative conditions [7–23] and (2) Jacobson's cyclization of thiobenzanilides [24]. Although these methods produce good results in many instances, there is still a demand to devolve new mild method for synthesis of benzthiazoles in the presence of cheap and bench top catalyst.

The use of water as a sole medium of organic reactions would greatly contribute to the development of environmentally friendly processes. In recent years much attention has been focused on acid-catalyzed organic reactions in water and several reactions of this type have been already identified [25].

Experimental

General

Chemicals including starting materials, solvents and sulfamic acid were obtained from Merck chemical company and used without purification. Melting points were obtained in open capillary tubes and also were measured on the Electrothermal 9100 apparatus. FT-IR spectra were recorded on a Perkin Elmer RXI spectrometer. NMR spectra were recorded on a Bruker Avance DPX 250 MHz instrument. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Deuterated solvents were used as lock and reference. Thin layer chromatography (TLC) was performed on SIL G/UV 254 plates.

General procedure for the synthesis of benzothiazoles in water

A mixture of an aromatic aldehyde (1 mmol) and 2-aminothiophenol (1 mmol) in water (2 mL) was stirred at room temperature in the presence of a catalytic amount of

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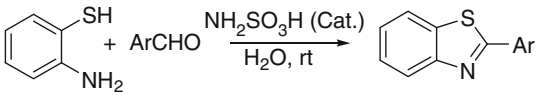
sulfamic acid (0.004 g, 0.04 mmol) for appropriate time (Table 2). The reaction was monitored by TLC (eluent: *n*-hexane/EtOAC: 7/3). After the reaction was completed, solid product was isolated by filtration and washed with water. The crud product was recrystallized from aqueous ethanol to give pure product. All of the products are known and were characterized by IR, ^{1}H NMR, and by melting point comparisons with those of authentic samples.

Results and discussion

In continuation of our study on the development of green synthetic methodologies [26, 27], herein we report a simple, efficient, environmentally benign and practical method for the synthesis of 2-arylbenzothiazoles from the condensation of 2-aminothiophenol with aromatic aldehydes in the presence of catalytic amount of sulfamic acid in water at room temperature (Scheme 1).

The synthesis of 2-arylbenzothiazole with this method is dependent on solvent and the amount of sulfamic acid (Table 1). The investigation of the reaction conditions for the synthesis of 2-(4-methoxy) phenyl benzothiazole from condensation of 2-aminothiophenol and 4-methoxybenzaldehyde demonstrated that 0.04 mmol of the catalyst in water at room temperature was optimal for obtaining the desired reaction (Table 1, entry 3). Interestingly, it was also observed that higher amount of catalyst did not improve the results (Table 1, entry 4–5); also, inferior results were



Scheme 1 Sulfamic acid catalyzed synthesis of 2-arylbenzothiazols

Table 1 Effect of solvent and catalyst evaluation in synthesis of 2-(4-methoxy) phenylbenzothiazole at room temperature

Entry	Solvent	Catalyst (mol%)	Time (min)	Yield (%)[a]
1	H_2O	None	120	Trace
2	H_2O	2	60	100
3	H_2O	4	25	100
4	H_2O	20	70	100
5	CH_3OH	4	22	100
6	EtOH	4	100	100
7	CH_3CN	4	50	100
8	*n*-Hexane	4	4 h	100
9	CH_2Cl_2	4	5 h	100

[a] Conversion

obtained with CH_3OH, EtOH, CH_3CN, CH_2Cl_2, Et_2O and *n*-hexane as solvents (Table 1, entries 6–9).

With the optimal conditions, the generality and the applicability of this method was further examined for the synthesis of 2-arylbenzothiazoles from condensation of 2-aminothiophenol with structurally diverse aromatic aldehydes including different type of substituted benzaldehydes, 1-naphthaldehyde, 2-naphthaldehde, 9-anthraldehyde and terephthaldehyde (Table 2).

The reaction proceeds smoothly to afford the desired products with good to excellent yields within short times. The substitution groups on the aromatic ring have no obvious effect on the yields and reaction time under the aforementioned optimal conditions. The condensation reactions of 2-aminophenol or katekol with aromatic aldehydes were not completed in the presence of catalytic amount of sulfamic acid in water under reflux conditions even after prolonged reaction times.

It should be noted that no added stoichiometric or excessive oxidant other than air was provided.

Interestingly, the catalyst is recycled at least three times without considerable loss in its activity; the turnover number (TON) and turnover frequency (TOF) for the sulfamic acid catalyst in the synthesis of 2-phenylbenzothiazole reached 92.5 and 57.8 h^{-1}, respectively (Table 2, entry 1).

To investigate the feasibility of applying this method on a preparative scale, we performed the synthesis of 2-phenylbenzothiazole on a 50-mmol scale of starting material. As expected, the reaction proceeded, similar to the case in a smaller scale (Scheme 2).

The proposed mechanism for the formation of 2-substituted benzothiazoles is shown in Scheme 3. It is proposed that sulfamic acid is a source for the formation of H^+, which makes the carbonyl and imine groups susceptible to nucleophilic attack. In the second step the actual oxidant is the oxygen of air, whereas in the atmosphere of nitrogen the reaction was not completed even after prolonged reaction times.

In order to learn the efficiency and greenness of this method, we compared our obtained results for the synthesis of 2-phenyl benzothiazole with the best of the well-known data from the literature (Table 3). As shown in the Table 3, many of the previously reported methodologies suffer from one or more disadvantages such as (1) requirement of excess oxidizing agents (entries 1–3, 8), (2) using high temperature or microwave-assisted baking (entries 1–6), (3) using transitional metal and corrosive catalyst (entries 1–6), (4) special efforts for the preparation of catalyst (entry 6), (5) prolonged reaction time (entries 1,7), (6) high load of catalyst (entries 4, 7), (7) using voltaic and toxic organic solvents (entries 1, 4,

Table 2 Sulfamic acid (0.04 mmol) catalyzed synthesis of 2-arylbenzthiazoles in water (2 mL) at room temperature from direct condensation of aromatic aldehydes (1 mmol) with 2-aminothiophenol (1 mmol)

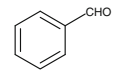
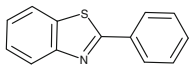
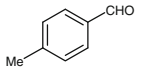
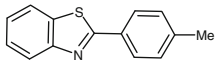
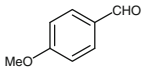
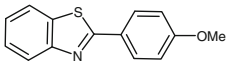
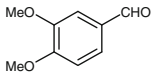
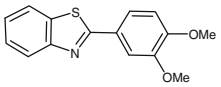
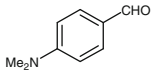
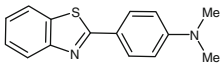
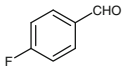
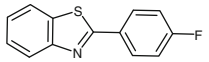
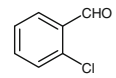
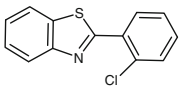
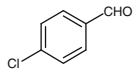
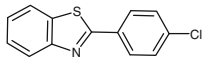
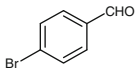
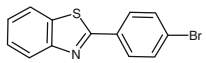
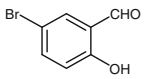
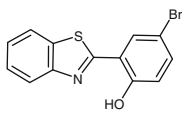
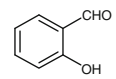
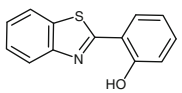
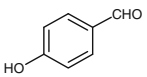
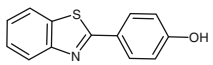
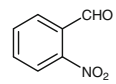
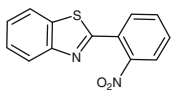
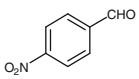
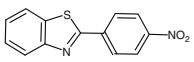
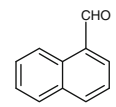
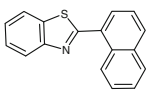
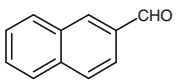
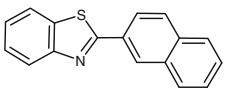
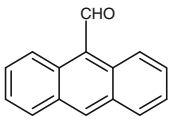
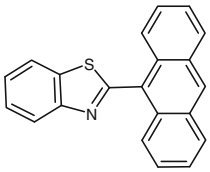
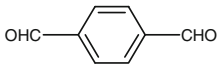
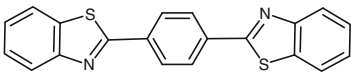
Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	Mp (°C) [Ref]
1			20, 23, 26, 26	96, 92, 93, 89[b]	218–219 [15]
2			25	78	79–81 [16]
3			25	94	121–122 [14]
4			25	96	135 [21]
5			40	93	173–174 [10]
6			37	89	100–101 [10]
7			45	81	80–82 [16]
8			40	89	115–117 [10]
9			40	92	133 [11]
10			25	95	164 [28]
11			20	96	130–131 [14]
12			25	94	227–229 [11]
13			25	90	121–122 [16]
14			30	97	229–230 [10]
15			30	93[c]	128–130 [11]
16			28	94	129–130 [13]

Table 2 continued

Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	Mp (°C) [Ref]
17			70	86[c]	218–221 [22]
18			100	83[c,d]	259–261 [23]

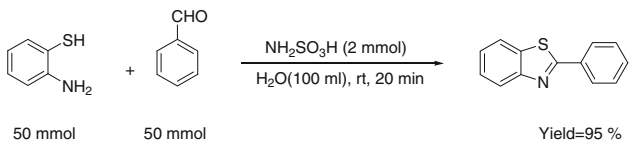
All the products are known and were characterized by IR, ^{1}H NMR and by melting point comparisons with those of authentic samples [7, 10, 11, 14, 21]

[a] Isolated yields

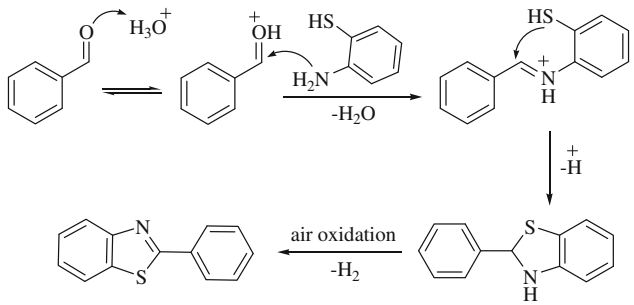
[b] Catalyst was reused for four times

[c] The reactions were performed in methanol

[d] Reaction conditions: in order to preparation of bis-benzthiazoles: 2-aminothiophenol (2 mmol), terephthaldehyde (1 mmol), sulfamic acid (8 mg, 0.08 mmol), MeOH (4 mL)



Scheme 2 Sulfamic acid catalyzed synthesis of 2-phenylbenzthiazole in large scale



Scheme 3 A plausible mechanism for synthesis of 2-arylbenzothiazols in the presence of catalytic amount of sulfamic acid

7). We believe that the present method helps avoid the disadvantages within the previously reported methodologies.

In summary, the significant advantages of this procedure are (a) the use of the eco-friendly, cost-effective, commercially available, reusable and chemically stable catalyst, (b) the procedure does not involve the use of any additional oxidants, (c) short reaction time, mild reaction conditions and very easy work-up, (d) avoiding hazardous and toxic solvent, (e) good to high yields of products, (f) practical large-scale synthesis of benzothiazols, (g) environmentally benign a chemical procedure both for academia and industry, (h) the procedure conforms to several of the guiding principles of green chemistry. All of these ensure an efficient route and provide an attractive and variable alternative to the previously reported procedures for the synthesis of 2-arylbenzthiazoles from condensation of aromatic aldehydes with 2-aminothiophenol.

Table 3 Comparison of the activity of various catalysts for the synthesis of 2-phenylbenzothiazole from the condensation of benzaldehyde and 2-aminothiophenol

Entry	Catalyst	Condition	Time (min)	Yield (%)	Reference
1	4-Methoxy-tempo (5 mol%), O_2 (1 atm)	Xylene, 100 °C	9 h	80	[6]
2	H_2O_2, CAN (10 mol%)	SF, 50 °C	13	97	[7]
3	H_2O_2, $Fe(NO_3)_3$ (10 mol%)	SF, 50 °C	4	97	[8]
4	I_2 (50 mol%)	DMF, 100 °C	25	88	[14]
5	$RuCl_3$ (5 mol%), air	[bmim]PF_6, 80 °C	30	83	[17]
6	$Cu_{3/2}PMo_{12}O_{40}$ (9 mol%), SiO_2	SF, M.W 1,350 W	15	95	[12]
7	Bakers' Yeast (2 g)	CH_2Cl_2, rt	24 h	75	[18]
8	$(NH_4)_2S_2O_8$ (10 mol%), SDS	water, rt	20	95	[19]
9	Sulfamic acid (4 mol%)	water, rt	20	96	Present work

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