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Research Article

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A facile and Rapid Access Towards the Synthesis of 2-aryl benzothiazoles using Succinimide-N-sulphonic Acid: A Reusable Catalyst

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Abstract: An efficient protocol has been developed for the preparation of a series of 2- arylbenzothiazole derivatives from condensation of 2-aminothiophenol with aromatic aldehyde using Succinimide-N-sulfonic acid (SuSA) as an efficient, cheap and reusable catalyst in solvent system and solvent-free grindstone method. These methods provide a simple and rapid protocol in terms of mild reaction conditions, clean reaction profiles and simple work-up procedure.

Keywords: Succinimide-N-sulfonic acid, 2-aminothiophenol, aromatic aldehyde, mild reaction conditions, Grind-stone method.

1. INTRODUCTION

The chemistry and biological study of heterocyclic compounds has been an interesting field for a long time in medicinal chemistry. A number of heterocyclic derivatives containing nitrogen and sulphur atom serve as a unique and versatile scaffolds for experimental drug design [1]. Benzothiazole is one of the most important heterocycle that has received overwhelming response owing to its diversified molecular design and remarkable optical, liquid and electronic properties [2]. Benzothiazoles and their derivatives are very important group of heterocyclic bicyclic systems [3-4], which play a fundamental role in organic and bioorganic chemistry. Benzothiazoles bearing substituents at C_2 position are of great interest as these structural frameworks have proved to be an important class of privileged bicyclic substructures owing to their potent utility as imaging agents for β-amyloid, antituberculotic, chemiluminescent agents, calcium channel antagonists, antitumor, antiparasitics and photosensitizers[5-12].

Because of their wide range of synthetic, industrial and pharmacological application, many

methods for the preparation of benzothiazole are reported in the literature. Among these methods are the condensation of 2-aminothiophenol with substituted nitriles, carboxylic acids, aldehydes, acyl chlorides or esters [13]. A number of catalysts namely, (PmIm)Br [14], TMSCl [15], I_2 [16], $ZrOCl_2 \cdot 8H_2O$ [17], PCC [18], H_2O_2, CAN [19], electro oxidation [20], Baker's yeast [21], PTSA [22], Dowex 50W reusable catalyst in water at 70 °C [23], TCCA in 2-MeTHF at ambient temperature [24], PEG,200/400 under microwave heating [25], NIBTS at ambient temperature under solvent free conditions [26], H_2SO_4/SiO_2 as a reusable catalyst at room temperature [27], H_2O [28], animal bone meal [29], $Na_2S_2O_5$ in refluxing DMF [30], $Cu(OAc)_2$/MCM41 supported catalyst under ultrasound irradiation [31], 2,4,6-trichloro-1,3,5-triazine under mild conditions [32], sulfamic acid [33], Glycerol as a solvent without catalyst [34], NH_4Cl [35], Silica sulfuric acid [36], $FeCl_3$/montmorillonite K-10 [37], $Sm(OTf)_3$[38-39] , Lithium bromide [40] and nano BF_3/SiO_2 [41].

However, many of these procedures suffer from one or more disadvantages such as harsh reaction conditions, prolonged reaction time period, poor yields with formation of many side products and use of large quantity of volatile organic solvents. So, the development of a clean, high yielding and ecofriendly approach is still desirable. As literature reveals that the 2-aryl benzothiazole derivatives are best synthesized in the presence of catalysts bearing sulfonic acid functionality, our efforts were directed for finding out sulphonic acid based organocatalysts, which should be mild in nature. In this endeavor, succinimide -N- sulphonic acid perfectly stood out as a mild acid catalyst. In recent years, succinimide-N-sulfonic acid (SuSA) has drawn much interest in different organic reactions due to its experimental simplicity. SuSA has shown considerable catalytic efficiency in different transformations [42-45].

In continuation of our ongoing research to develop novel methodologies in synthetic chemistry [46-47], we have investigated here an efficient, low cost, and environmentally benign protocol for the synthesis of 2-arylbenzothiazole using succinimide-N-sulfonic acid (SuSA) a simple, reusable and inexpensive catalyst in solvent system and solvent-free grindstone method.

2. EXPERIMENTAL

All chemicals were of analytical grade, purchased from commercial source and used directly. Melting points were recorded by the open tube capillary method and are uncorrected. The progress of the reaction and the purity of compounds were monitored by thin-layer chromatography (TLC) analytical silica gel plates (Merck 60 F_{250}). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance (400 and 100 MHz, respectively) instrument in $CDCl_3$ solvent, chemical shifts are given in δ ppm relative to tetramethylsilane (TMS) and coupling constants (*J*) are expressed in Hertz (Hz).

2.1. Preparation of Succinimide-N-sulfonic acid

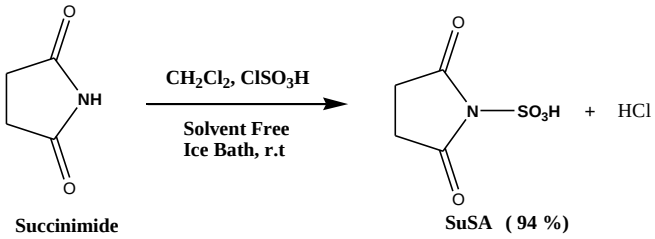
Succinimide-N-sulphonic acid as a stable reagent is easily prepared as reported by the reaction of succinamide with chlorosulphonic acid (Yield 94%) Scheme-1 [41].

2.2. General procedure for the preparation of 2-aryl benzothiazole (3a-m)

A. Conventional method:

SuSA (10 mol %) was added to a stirred solution of the aldehyde (1 mmol) and 2-aminothiophenol (1 mmol) in acetonitrile (5 mL) and the mixture was stirred at room temperature for appropriate time (Table 2). After completion of the reaction monitored by TLC (Ethyl acetate: Hexane, 8:2), the solvent was

removed under reduced pressure and ethyl acetate (5 mL) was added, and the catalyst was recovered by filtration and washed with ethyl acetate (5 mL). The filtrate was washed with water and then dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure provided the crude products with high purity, if required; a recrystallization was performed from ethanol in some cases.



Scheme-1 Preparation of succinimide-N-sulfonic acid

B. Grindstone method:

A mixture of aldehyde (1 mmol), 2-aminothiophenol (1 mmol) and SuSA (10 mol %) was crushed in a mortar with a pestle at room temperature. Progress of the reaction was monitored by TLC. After completion of the reaction (7-15 min.), to the crude product ethyl acetate (5 mL) was added, and the catalyst was recovered by filtration and washed with ethyl acetate (5 mL). The filtrate was washed with water and then dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure provided the crude products with high purity, if required; a recrystallization was performed from ethanol in some cases.

2.3. Spectral data of selected compounds

Compounds 3b, 3d, 3e, 3f, 3g, 3h, 3k-m are previously reported in the literature and data matches with literature data [37-41].

2.3.1. 2-Phenyl-1,3-benzothiazole (3a)

IR (KBr): *v/max* 3060, 3020, 1609, 1590 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.07 (m, 3H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.47 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 154.1, 135.1, 133.6, 130.9, 129.0, 127.6, 126.3, 125.2, 123.2, 121.6.

2.3.2 2-(4-Chlorophenyl)benzothiazole (3c)

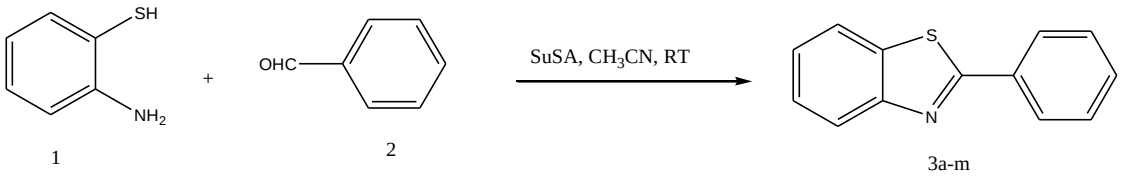
IR (KBr pallets):*V*max 3081, 3032, 1613, 1593 cm-1; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 154.0, 137.0, 135.0, 132.1, 129.2, 128.7, 126.5, 125.4, 123.3, 121.6.

2.3.3 2-(4-Methylphenyl) benzothiazole (3i)

IR (KBr pallets):*V*max 3026, 2811, 2343, 1606, 1581, 1520 cm^{-1}.^1H NMR (300 MHz, $CDCl_3$): δ8.00-8.06 (m,3H), 7.96 (d, 1H,*J* = 8.0 Hz),7.51 (t,1H, *J* = 8.4 Hz), 7.41 (t,1H, *J* = 8.4 Hz), 7.36 (d,2H, *J* = 8.1 Hz) and *δ* 2.45 (s,3H)^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 154.2, 141.6, 135.0, 131.0, 129.7, 127.3, 126.2, 125.0, 122.9, 121.6 and 21.2. MS (EI, m/z): 225.40 [M^+].

2.3.4 2-(4-N,N Dimethylphenyl) benzothiazole (3j)

IR (KBr)*/υ*: 3355, 2358, 1598, 1478, 1210, 1017, 965, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (t, *J* = 8.7 Hz, 3H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 3.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 154.4, 152.2, 134.5,128.9, 126.0, 124.2, 122.3, 121.4, 121.3, 111.7, 40.1.



1 2 3a-m

Scheme 2. Synthesis of 2-arylbenzothiazoles

Table 1. Effect of solvent and catalyst evaluation in synthesis of 2-phenylbenzothiazole at room temperature[a]

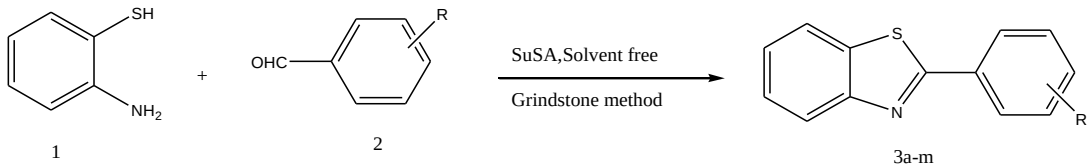
Entry	Solvent	Catalyst (mol %)	Time (min.)	Yield[b] (%)
1	CH_3CN	------	60	Trace
2	CH_3CN	5	25	82
3	CH_3CN	7	15	90
4	CH_3CN	10	5	94
5	CH_3CN	20	10	94
6	H_2O	10	30	85
7	EtOH: H_2O	10	25	88
8	EtOH	10	20	90
9	CH_3OH	10	20	92
10	CH_2Cl_2	10	60	75

[a] *Reaction conditions: benzaldehyde(1 mmol), 2-amino- thiophenol (1 mmol), SuSA (10 mol%) at room temperature.*

[b] *Isolated yield. Bold row is the standard optimization condition*

3. RESULTS AND DISCUSSION

To explore the use of succinimide-N-sulfonic acid as a catalyst, reaction of benzaldehyde and 2-aminothiophenol for the preparation of 2-arylbenzothiazole compound **3a-3m** was considered as a standard model reaction (Scheme 2). Model reaction in the absence of catalyst did not lead to desired product formation. It means intervention of catalyst was must for initiation of the reaction. To determine exact requirement of catalyst for the reaction, we investigated the model reaction using different concentrations of Succinimide-N-sulfonic acid (Table 1). During this study, we observed that, 10 mol% Succinimide-N-sulfonic acid proved to be an efficient catalyst to carry out the reaction smoothly.



1 2 3a-m

Scheme 3. Synthesis of 2-arylbenzothiazoles

The model reaction was further investigated using different solvents. Whether, the reaction rate could be accelerated and the product yield could be enhanced. During this study solvents like acetonitrile,

ethanol, methanol, water, aqueous ethanol and dichloromethane were tested but, use of acetonitrile proved to be suitable solvent (Table 1). Encouraged by this result, in further set of experiments, in order to build the generality of the reaction, variety of aromatic aldehydes with either electron-donating or electron-withdrawing groups were converted to 2-arylbenzothiazole derivatives in good to excellent yields. All the results are summarized in Table 2.

In order to reduce or replace the volatile organic solvents from the reaction medium, we further studied the same reaction under solvent-free grindstone method using mortar and pestle; we found that yields of the products were high as compared to the solvent system method (Scheme 3).

Table 2. Synthesis of 2-arylbenzothiazole in the presence of SuSA

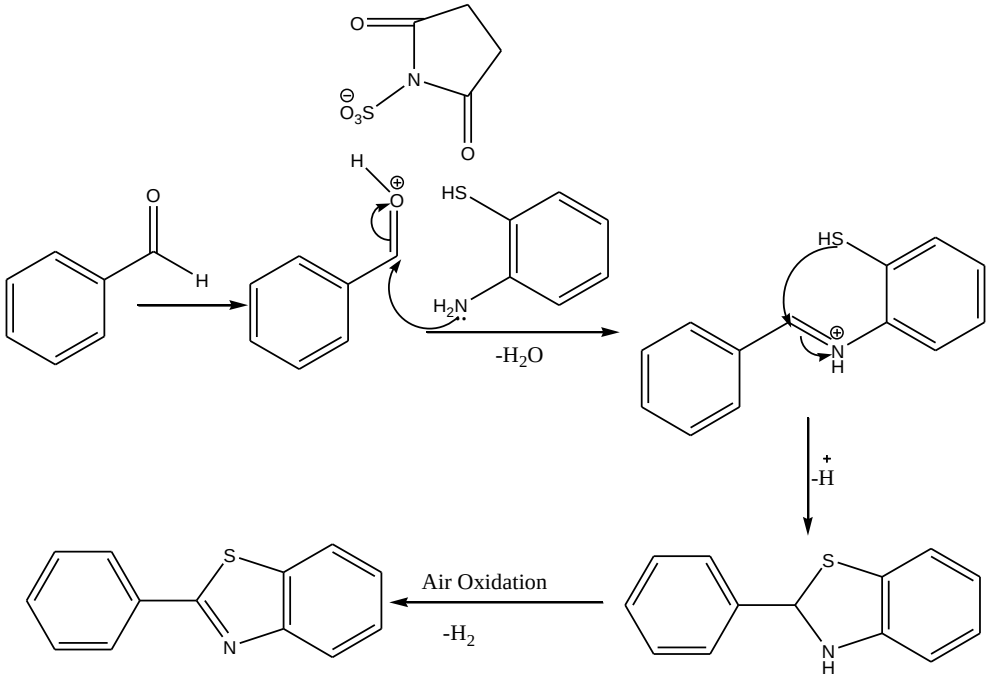
Entry	Aldehyde	Conventional Method[a]		Grinding Method[b]	Melting point[d] ^{O}C [Ref.]
		Time (min.)	Yield[c](%)	Yield[c] (%)	
3a	C_6H_5-CHO	5, 5, 7, 10	94, 90, 88,85[e]	94	112-114[34]
3b	4-CH_3O-C_6H_4-CHO	5	91	94	122-124[34]
3c	4-Cl-C_6H_4-CHO	5	92	95	115-116[34]
3d	4-NO_2-C_6H_4-CHO	6	92	95	228–230[40]
3e	4-BrC_6H_4-CHO	5	90	92	128-130[39]
3f	2-OH C_6H_4-CHO	8	84	86	126–128[33]
3g	3-$NO_2C_6H_4$-CHO	7	90	92	198-201[40]
3h	2-$CH_3OC_6H_4$-CHO	8	85	90	102-104[35b]
3i	4-Me-C_6H_4-CHO	6	91	94	82-84 [40]
3j	4-N(Me)$_2C_6H_4$-CHO	7	92	94	170-172[33]
3k	4-Pyridyl-CHO	10	80	85	130-132[39]
3l	2-Cl C_6H_4-CHO	8	84	88	80-82 [33]
3m	2-NO_2 C_6H_4-CHO	7	90	92	120-122[33]

[a] *Reaction of aldehyde 1 (1 mmol), 2-aminothiophenol 2 (1 mmol), and SuSA (10 mol %) in acetonitrile (5 mL), stirring at room temperature.*
[b]*Reaction of aldehyde 1 (1 mmol), 2-aminothiophenol 2 (1 mmol), and SuSA (10 mol %) under solvent-free grindstone method.(7-15 min)*
[c]*Isolated yields*
[d]*Melting points matches with literature values.*
[e]*Catalyst was reused for three times*

In order to learn the efficiency and greenness of these methods, 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 requirement of excess oxidizing agents, using high temperature or

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 (mol %)	Condition	Time (min.)	Yield (%)	[Ref.]
1	H_2O_2, CAN (10 mol%)	SF, 50 ^oC	13	97	[19]
2	I_2 (50 mol %)	DMF, 100 ^oC	25	88	[16]
3	Baker's Yeast (2 g)	CH_2Cl_2, rt	24h	75	[21]
4	LiBr (10 mol %)	EtOH,))))) / Δ or conventional	10/35	94/82	[40]
5	PTSA (10 mol %)	Water, 70^oC	60	95	[22]
6	Sulfamic acid (4 mol%)	Water, rt	20	96	[33]
7	$Sm(OTf)_3$	EtOH:H_2O, 50-60^o C	120	89	[38]
8	SuSA (10 mol %)	Acetonitrile, rt	5	90	**(**Present work)
9	SuSA (10 mol %)	Solvent-free gridstone method	7	94	**(**Present work**)**



Scheme 4. A plausible mechanism for synthesis of 2-arylbenzothiazols in the presence of Succinimide-N-sulfonic acid

microwave-assisted, prolonged reaction time, high load of catalyst, using volatile and toxic organic solvents. We believe that the present method helps to avoid the disadvantages within the previously reported methodologies.

The reusability of the catalyst is one of the most important benefits and makes it useful for commercial applications. Thus the, recovery and reusability of SuSA were investigated. In order to exhibit the recyclability of the SuSA, the reaction of benzaldehyde and 2-aminothiophenol was selected again as a model. After reaction completion, the SuSA was washed with ethyl acetate, dried and stored for another consecutive reaction runs. This process was repeated for three runs and no appreciable loss of yield was observed. Almost consistent activity was observed over three runs and desired products were obtained in high yields after 1-3 runs, respectively (Table 2 Entry 3a). It means that catalyst is stable and reused without significant loss of efficiency.

4. CONCLUSION

In summary, in this paper we report synthesis of 2-arylbenzothiazoles form the condensation of 2-amniothiophenol and various types of aromatic aldehydes catalyzed by succinimide-N-sulfonic acid in solvent system and solvent-free grindstone method. Mildness of the reaction conditions, short reaction times, high to excellent yields, easy workup and reusability of the catalyst are noteworthy advantages of these methods. Further applications of SuSA on the extension of this protocol are ongoing in our laboratory.

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The authors declare no conflict of interest

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