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One-pot synthesis of 1,3-benzo[*d*]thiazole derivatives promoted by $Al(HSO_4)_3$ under sonication conditions

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ABSTRACT

$Al(HSO_4)_3$ is an efficient, readily available and cheap catalyst for the synthesis of 1,3-benzo[*d*]thiazole derivatives by condensation of 2-aminothiophenol and aldehydes under sonication conditions. This protocol is very simple with easy workup and good to excellent yields of products.

***Keywords**: 1,3-Benzo[d]thiazole, Benzothiazoles, $Al(HSO_4)_3$, Aluminum hydrogen sulfate, 2-Aminotiophenol, Sonication conditions.*

1. Introduction

The presence of an imidazole ring in natural products and pharmacologically active compounds has instituted a diverse array of synthetic approaches to these heterocycles. Benzothiazole derivatives have many biological and pharmaceutical application such as probes for the 5HT1A receptor, serotonin transporter (SERT) [1], antitumor [2], histone deacetylase inhibitor [3], anticancer activity [4-7], anti-tubercular [8], antimicrobial [9,10], antibacterial [11], anti-inflammatory and anti-nociceptive [12], fungicidal [13] neurotoxicity and anticonvulsant [14], cytotoxic [15], analgesic [16], cyclin-dependent kinases (CDK2) inhibitors [17], potent S1P1 agonists with in vivo lymphocyte-depleting activity[18], inhibitors of thrombin and trypsin IV [19], adenosine A2B receptor antagonists [20], for imaging of amyloids [21] and inhibitors of beta-glucuronidase [22]. Optical properties such as dye sensitized solar cells [23], fluorescent probe for thiol bioimaging [24], fluorescent DNA intercalators for studying Alzheimer abeta1-42 and prion amyloid peptides [25] as potential radiotracers for *β*-amyloid plaques in Alzheimer's disease [26], photosensitizing agents [27], and alkyne fluorescent sensor for Cu detection in living cell [28] have been found for some benzothiazole derivatives. Some benzothiazoles have liquid crystalline [29,30] and ionic liquid [31] properties. Benzothiazoles have been synthesized *via* a two component coupling of 2-aminothiophenol with gem-dibromomethylarenes [32], carboxylic acids [33] or aldehydes. Previously many catalysts have been applied for the latter protocol such as ZnO-beta zeolite [34], molecular iodine [35], $NaHSO_4.SiO_2$ [36], SiO_2 in microwave [37], *p*-toluenesulfonic acid [38], $Co(NO_3)_3/H_2O_2$ [39], montmorillonite K10 [40], acetic acid [41], ceric ammonium nitrate (CAN) [42] and oxalic acid, silica sulfuric acid or $AlCl_3$ [43].

Very recently, we among many others have demonstrated that heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and minimization of chemical wastes as compared to the liquid phase counterparts. Thus, inorganic acidic salts such as $Al(HSO_4)_3$, $Mg(HSO_4)_2$ and $Zr(HSO_4)_4$ could be recommended for above mentioned purposes. $Al(HSO_4)_3$ is prepared *via* reaction of aluminum chloride with concerted sulfuric acid. Previously, this catalyst was used for promotion of Friedel–Crafts acylation [44], xanthene synthesis [45] and acetylation, formylation, and oxidation of alcohols [46-48].

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2. Experimental

2.1. General

The chemicals were used without any additional purification. The products were characterized by FT-IR, ^{1}H NMR, and a comparison of their physical properties with those reported in the literature. FT-IR spectra were run on a Bruker, Eqinox 55 spectrometer. A Bruker (DRX-400 Avanes) NMR was used to record the ^{1}HNMR spectra. Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus. BANDELIN Sonopuls HD 3200 ultrasonic apparatus (20 kHz, 150 W) was used for sonication. The microwave oven Kenwood, 1300W and Mixer Mill (MM 400) in 25 Hz frequency were used for running the described reactions.

2.2. General procedure for the synthesis of 1,3-benzo[d]thiazole derivatives

A mixture containing of 2-aminothiophenol (1 mmol), aldehyde (1 mmol) and $Al(HSO_4)_3$ (0.02 g) dissolved in ethyl acetate (5 mL), was exposed under ultrasound irradiation. The progress of the reaction was monitored by TLC. After completion of the reaction, ethyl acetate was evaporated in vacuum and the obtained solid dissolved in acetone followed by addition of water. The obtained solid product was recrystallized in hot ethanol. All the products are known and were identified by comparison of their physical and spectral data with those of authentic samples.

3. Results and Discussion

The reaction of benzaldehyde (1 mmol) with 2-aminothiophenol (1.2 mmol) was investigated for optimization of the reaction conditions (Table 1). We have found that the best condition was sonication condition in ethyl acetate and a molar ratio of benzaldehyde: 2-aminothiophenol: $Al(HSO_4)_3$ equal to 1:1:0.06. The reusability of the $Al(HSO_4)_3$ catalyst was also examined and no reusability was observed.

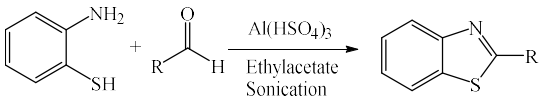
Table 1. Synthesis of 2-phenyl, 1,3-benzo[*d*]thiazole under various conditions.[a]

Entry	Catalyst (g)	Solvent	Conditions	Time (min)	Yield (%)	Ref.
1	$Al(HSO_4)_3$(0.01)	-	r.t	20	50	-
2	$Al(HSO_4)_3$ (0.02)	-	r.t	20	57	-
3	$Al(HSO_4)_3$(.03)	-	r.t	20	60	-
4	$Al(HSO_4)_3$(0.01)	-	60°C	10	63	-
5	$Al(HSO_4)_3$(0.01)	-	80°C	10	74	
6	$Al(HSO_4)_3$(0.02)	-	60°C	10	80	-
7	$Al(HSO_4)_3$(0.02)	-	80°C	10	91	-
8	$Al(HSO_4)_3$(0.02)	EtOAc	Sonication	20	93	
9	$Al(HSO_4)_3$(0.02)	EtOH	Reflux	180	20	-
10	$Al(HSO_4)_3$(0.02)	EtOAc	Reflux	120	55	-
11	$Al(HSO_4)_3$(0.02)	*n*-Hexane	Reflux	240	35	-
12	$Al(HSO_4)_3$(0.02)	MeOH	Reflux	360	40	-
13	$Al(HSO_4)_3$(0.02)	CH_3Cl	Reflux	90	45	-
14	$Al(HSO_4)_3$(0.02)	-	M.W.	5	60	-
15	$Al(HSO_4)_3$(0.02)	-	Mixer Mill	60	54	-
16	PTSA(10mol%)	H_2O	70°C	60	97	[38]
17	$Co(NO_3)_2.6H_2O$	DMF	80°C	35	88	[39]
18	CAN	MeOH	r.t.	Overnight	75	[42]
19	Silica Sulfuric Acid	-	M.W.	12	90	[49]
20	Silica Sulfuric Acid	CH_3CN	80°C	25	82	[43]
21	Oxalic acid	$EtOH/H_2O$	80°C	30	80	[43]
22	$AlCl_3.6H_2O$	MeOH:H_2O (20:1)	r.t.	30	90	[43]
23	Montmorillonite K10	$PhNO_2$	M.W.	5	92	[40]
24	Acetic acid	Acetic acid	Reflux	300	76	[41]

The applicability of the present method to a large scale process was examined with 10 mmol of benzaldehyde and 12 mmol of 2-aminothiophenol under sonication conditions in ethyl acetate which gave 2-phenyl-benzothiazole in 83% yield. 2-aminothiophenol and various aldehydes were used as substrates for the synthesis of benzothiazoles under sonication conditions in ethyl acetate (Scheme 1 and Table 2). For synthesis of benzo[*d*]thiazole, we have used trioxane as formaldehyde source (Table 2, entry 6). The aromatic aldehydes containing electron releasing or electron withdrawing groups have reacted in this protocol with high yields. In this protocol, many aliphatic aldehydes were examined but oily liquids with difficult purification method were obtained.

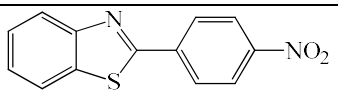
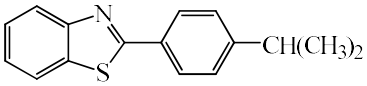
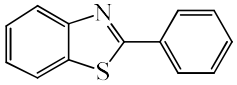
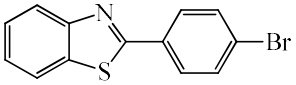
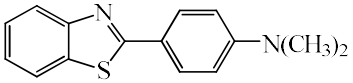
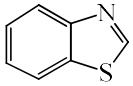
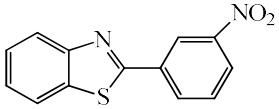
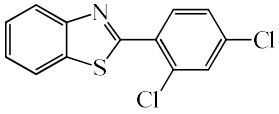
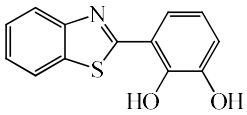
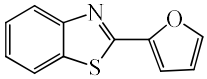
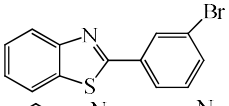
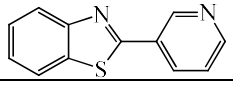
4. Conclusions

We have demonstrated a simple method for the synthesis of 1,3-benzo[*d*]thiazoles with using $Al(HSO_4)_3$ as eco-friendly and efficient catalyst under sonication condition. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are some advantages of this protocol.



Scheme 1.

Table 2. Synthesis of 2-substituted benzothiazoles in the presence of $Al(HSO_4)_3$ under sonication conditions.[a]

Entry	Product	Yield%	m.p. (°C)		Ref.
			Found	Reported	
1		90	227-228	224-225	[42]
2		77	65-67	-	
3		93	112-113	111-112	[43]
4		85	132-134	133-134	[43]
5		80	169-171	173	[52]
6		71	80-81	-	
7		84	181-183	184-186	[42]
8		83	133-134	-	[50]
9		75	179-181	-	[50]
10		76	102-103	103	[51]
11		83	81-83	82-83	[43]
12		76	113-115	-	[50]

[a]A mixture of 2-aminothiophenol (1.2 mmol), aldehyde (1 mmol), $Al(HSO_4)_3$ (0.02 g) and ethylacetate (5 mL) was refluxed in sonication condition for 20 minutes.

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