

Research Article

Regioselective Thiocyanation of Aromatic and Heteroaromatic Compounds Using [2-(Sulfooxy)ethyl]sulfamic Acid as an Efficient, Recyclable Organocatalyst and Novel Difunctional Brønsted Acid

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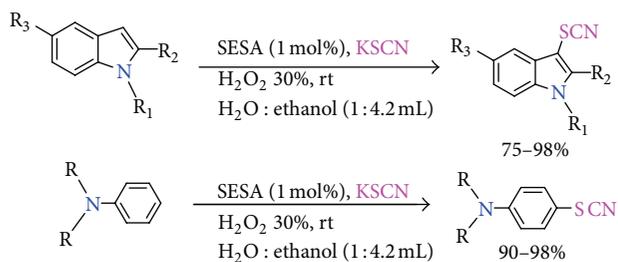
A green and simple procedure for the thiocyanation of aromatic and heteroaromatic compounds is described. [2-(Sulfooxy)ethyl]sulfamic acid (SESA) (supported on silica) is easily produced by addition of chlorosulfonic acid to 2-aminoethanol and this catalyst is applied as an efficient, reusable, and heterogeneous catalyst for the thiocyanation of heterocycles, substituted anilines (electron-rich and electron-deficient), and *N,N*-disubstituted aromatic amines using hydrogen peroxide in the water: ethanol as a solvent at room temperature. The catalyst can be easily recovered and reused for five reaction cycles without considerable loss of activity.

1. Introduction

The importance of minimizing the impact that chemical processing has on the environment is growing, with an increased appreciation of the need to reduce pollution and depletion of our finite environmental resources. Optimal use of material and energy and an efficient waste management can be recognized as important factors for environmental protection. To realize this goal, in recent years, significant articles have appeared reporting efficient solvent-free reactions by grinding [1–3]. This technique has many advantages such as reduced pollution, low cost, process simplicity, and easier workup. In addition, from the green and environmental acceptability, recently more attention has been paid to the application of inorganic acidic salts in organic synthesis [4, 5]. Solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal in different chemical processes. Also, wastes and byproducts can be minimized or avoided by using solid acids in developing cleaner synthesis routes.

The electrophilic thiocyanation of aromatics and heteroaromatics is an important carbon-heteroatom bond-forming reaction in organic synthesis. Organocatalysis has emerged during the last decade as one of the major issues in the development of catalytic chemical technology [6]. As for conventional catalysis with transition metal complexes, by using organic catalysts large quantities of products are expected to be prepared using a minimal amount of small organic molecules [7, 8]. The recent organocatalytic protocols are particularly attractive because of the mildness of the reaction conditions, operational simplicity, the potential for the development of large-scale production, and the ready availability and low toxicity of the organocatalysts [9, 10]. Organocatalyzed reactions using water as a solvent have attracted a great deal of attention mainly because of the low cost, the safety, and the environmentally benign nature of water. The synthesis of organic molecules via reactions in water is an extensively investigated topic, which entails the additional challenge of water tolerance for a catalyst.

Thus, the development of small organic molecules that catalyze reactions in water is currently an important goal



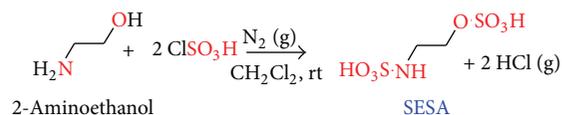
SCHEME 1: Thiocyanation reaction of indole and *N,N*-disubstituted aniline in the presence of [2-(sulfooxy)ethyl]sulfamic acid (SESA).

amongst today's synthetic community [11]. The thiocyanation reaction is one of the most useful carbon-sulfur bond-forming reactions. Thiocyanates have gained considerable importance in various areas of organosulfur chemistry [12]. For example, the thiocyanate group occurs as an important functionality in certain anticancer natural products formed by deglycosylation of glucosinolates derived from cruciferous vegetables [13–17]. On the other hand, thiocyanosubstituted compounds are a useful precursor for the synthesis of organosulfur compounds, in which the thiocyanate group will be readily transferred to other functional groups such as sulfide [13], aryl nitrile [17], thiocarbamate [18, 19], and thionitrile [20]. Several methods have been developed for the thiocyanation of arenes by using various reagents [21–23] such as *N*-thiocyanatosuccinimide [24], ceric ammonium nitrate (CAN) [25], acidic montmorillonite K10 clay [26], iodine/methanol [27], diethyl azodicarboxylate [28], IL-OPPh₂ [29], pentavalent iodine [30], IBX [31], FeCl₃ [32], potassium peroxydisulfate-copper(II) [33], and Selectfluor [34]. However, most of the reported methods for the synthesis of aryl thiocyanates are associated with one or more of the following drawbacks such as use of strongly acidic or oxidizing conditions, high temperatures, low yields, long reaction times, the use of large amounts of catalyst, and the use of toxic or expensive catalysts. Thus, the search for finding an efficient, inexpensive, and nonpolluting method for the synthesis of this class of compounds is still of practical importance.

Because of these problems and the recent intense attention to environmentally benign protocols, the search for new and efficient catalysts that are able to promote organic reactions under green conditions is of interest for the production of aryl thiocyanates. In continuation of our study on application of solid acid [35–42], we report the synthesis of organothiocyanate derivatives in the presence of a catalytic amount of [2-(sulfooxy)ethyl]sulfamic acid (SESA) as a novel, efficient, and recyclable organosolid acid catalyst in ethanol/water (Scheme 1).

2. Experimental

All chemicals were purchased from Merck or Fluka Chemical companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions



SCHEME 2: Synthesis of [2-(sulfooxy)ethyl]sulfamic acid (SESA).

was monitored by TLC using silica gel SIL G/UV 254 plates. The ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) were run on a Bruker Avance DPX-250 FT-NMR spectrometer (*d* in ppm). Microanalysis was performed on a PerkinElmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus using open capillary tubes.

2.1. Preparation of [2-(Sulfooxy)ethyl]sulfamic Acid (SESA). A 50 mL suction flask was equipped with a constant-pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. 2-Aminoethanol (1.527 g, 25 mmol) was charged in the flask and chlorosulfonic acid (5.83 g, ca. 3.4 mL, 50 mmol) was added dropwise over a period of 1 h at room temperature. HCl evolved immediately. After completion of the addition, the mixture was shaken for 80 min, while the residual HCl was eliminated by suction. Then, the mixture was washed with diethyl ether (or CH₂Cl₂) to remove the unreacted chlorosulfonic acid (¹H NMR spectrum of BSA in acetone-*d*₆ showed a broad absorption at 12.22 ppm) and then 10.84 g SiO₂ was added and mixed. Finally, a grayish solid material (solid acid) was obtained in 98% yield (5.42 g SESA + 10.84 SiO₂, W_{SESA} : W_{SiO₂}, 1 : 2).

2.2. General Procedure for Preparation of Thiocyanation Reaction (1b). A suspension of indole (0.117 g, 1 mmol), potassium thiocyanate (0.294 g, 3 mmol), and SESA/SiO₂ (0.02 g, 3 mol%) in H₂O : ethanol (1 : 4, 2–5 mL) was stirred at room temperature for 5 min. Then, H₂O₂ (30%) (3 mmol) was added dropwise (2–5 min). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with CHCl₃ (2 × 25 mL). Anhydrous Na₂SO₄ (3 g) was added to the organic layer and filtered off after 20 min. CHCl₃ was removed. The yield was 0.159 g, (91%), m.p 71–73°C. FT-IR (KBr): 2159, 3289, ¹H-NMR (FT-300 MHz, CDCl₃/TMS): δppm 8.87 (br s, 1H, NH), 7.83 (1H, *d*, *J* = 8.8 Hz), 7.46–7.23 (4H, m). ¹³C NMR (75 MHz, CDCl₃): 136.06, 131.22, 127.66, 123.83, 121.87, 118.65, 112.24, 91.76.

3. Results and Discussion

[2-(Sulfooxy)ethyl]sulfamic acid (SESA) was easily prepared by addition of chlorosulfonic acid to 2-aminoethanol under N₂ atmosphere at room temperature. This reaction was easy and clean because HCl gas was evolved from the reaction vessel immediately (Scheme 2). We examined the catalytic ability of SiO₂/HO₃SOCH₂CH₂NHSO₃H for thiocyanation regioselectivity reaction to corresponding thiocyanated compounds N–SiO₃H.

TABLE 1: Optimization amounts of SESA, H₂O₂, and KSCN in water : ethanol (1 : 4, 5 mL).

Entry	SESA %	H ₂ O ₂ (mmol)	KSCN (mmol)	Time (min)	Yield %
1	—	3	3	12 (h)	—
2	1	3	4	10	92
3	3	3	3	30	90
4	1	4	3	2	97
5	5	3	3	10	93
6	5	2	3	50	65
7	5	4	3	10	88
8	10	3	4	20	92
9	10	3	3	15	91
10	15	3	3	10	90
11	5	2	3	60	55
12	5	3	2	5 (h)	60
13	5	—	—	24 (h)	—

SESA was similarly produced as in our previous report [37–40]. The product was identified by its spectral data. IR spectrum showed the characteristic peak of S–O group at 450–600 cm⁻¹, S=O at 1000–1200 cm⁻¹, and broad peak at 2900–3600 cm⁻¹ related to the OH of SO₃H groups. Moreover, the two peaks observed at 1085 cm⁻¹ and 1285 cm⁻¹ correspond to vibrational modes of N–SO₂ bond.

The IR spectrum of the catalyst showed a broad peak at 3100–3400 cm⁻¹. ¹H NMR spectrum of SESA showed the unmistakable acidic hydrogens (SO₃H) peaks at 12.86 and 11.96, peak of NH group at 9.806, peak of O–CH₂ group between 3.417 and 3.442, peak of N–CH₂ group between 3.809 and 3.840, and peak of NH group at 9.806. These spectrums confirmed that this catalyst was exactly synthesized.

The thiocyanation was investigated at various conditions. In the absence of SESA, reaction was not accomplished (Table 1, entry 1). For the synthesis of aryl thiocyanate, conversion of indole into its corresponding indole thiocyanate in water : ethanol (1 : 4) and room temperature has been considered as a model reaction (Scheme 1).

In an initial experiment, we examined the reaction of indole in H₂O/C₂H₅OH in various ratios of H₂O₂ and KSCN (the results are summarized in Table 1). As Table 1 indicates, a ratio of 1 : 3 : 3 (indole : H₂O₂ : KSCN) was found to be the most suitable in presence of SESA 1%. In the absence of catalyst when indole was treated with hydrogen peroxide and KSCN, no product was obtained.

When the amount of catalyst was less than 1 mol%, the yield of product was reduced. Otherwise, increasing the catalyst loading from 1 to 15 mol% does not significantly change the yield. Also, the solvent effect was investigated using indole as a substrate. We carried out the reaction with the same concentration of the reactants in H₂O, EtOH, MeOH, CH₃CN, CH₂Cl₂, THF, and AcOEt. Both the yields and the reaction times listed in Table 2 suggested that H₂O : ethanol (1 : 4, 2 mL) was the most favorable solvent for

TABLE 2: Optimization of solvent in presence of SESA (1 mol%) for synthesis of 3-thiocyanato-1H-indole 1b.

Entry	Solvent	Time (min)	Yield %
1	H ₂ O (5 mL)	120	65
2	Ethanol (5 mL)	20	78
3	H ₂ O : ethanol (1 : 1, 5 mL)	35	76
4	H ₂ O : ethanol (1 : 1, 10 mL)	50	74
5	H ₂ O : ethanol (1 : 2, 5 mL)	40	81
6	H ₂ O : ethanol (1 : 3, 5 mL)	30	84
7	H ₂ O : ethanol (1 : 4, 5 mL)	20	93
8	H ₂ O : ethanol (1 : 4, 2 mL)	2	97
9	H ₂ O : ethanol (1 : 5, 5 mL)	20	88
10	H ₂ O : ethanol (1 : 10, 5 mL)	20	87
11	H ₂ O : ethanol (2 : 1, 5 mL)	40	84
12	H ₂ O : ethanol (5 : 1, 5 mL)	70	82
13	H ₂ O : ethanol (2 : 3, 5 mL)	50	63
14	MeCN	150	69
14	MeOH	60	83
15	CH ₂ Cl ₂	150	45
16	THF	150	65
17	AcOEt	150	45

the thiocyanation in presence of SESA. Consequently, 1 mol% SESA was used in subsequent experiments.

We specified that H₂O : EtOH (1 : 4) was the best and most suitable solvent for the thiocyanation of aromatic and heteroaromatic compounds in the presence of SESA.

After obtaining the optimal conditions, we carried out the reaction with various aromatic and heteroaromatic compounds under the optimized conditions (the results are summarized in Table 3). A good range of aromatic and heteroaromatic compounds underwent thiocyanation with high regioselectivities and this reaction provided good-to-excellent yields with all the substrates tested.

The reaction was mild and equally good for indoles and *N,N*-disubstituted anilines. As shown in Table 3, indole and electron-rich indoles gave the desired products in excellent yields (Table 3, entries 1–3). Also, electron-deficient indoles such as 5-bromoindole afforded the corresponding 5-bromo-3-thiocyanatoindoles in good yields but required longer reaction times (Table 3, entry 5). This observation can be attributed to the lower electron density of such substrates. The thiocyanation reaction was highly regioselective at the 3-position of the indole ring and *para*-position in *N,N*-disubstituted anilines.

After reviewing the reactions for the heterocycles, we examined the capability of aromatic amines in the thiocyanation reaction. The substrate reacted and produced corresponding aryl thiocyanates in high yield (Table 3, entries 6–11), but *N,N,N*-trimethylaniline, 1-phenylpiperazine, aniline, *o*-toluidine, and *N,N,N*-triphenylamine did not react with potassium thiocyanate and SESA/H₂O₂ to afford the corresponding derivatives (Table 3, entries 13–16).

TABLE 3: Substrate scope in the thiocyanation reaction of arenes using KSCN/SESA/H₂O₂ under room temperature.

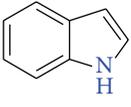
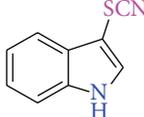
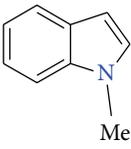
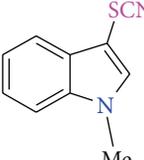
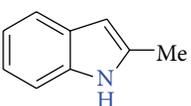
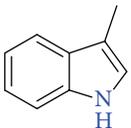
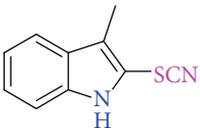
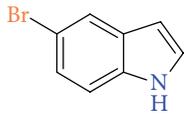
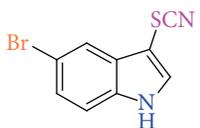
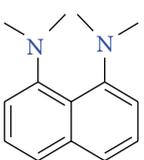
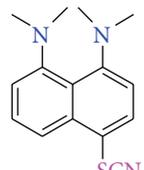
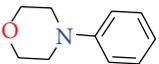
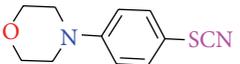
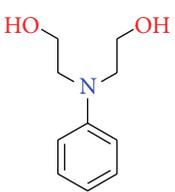
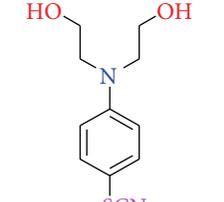
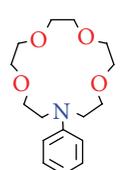
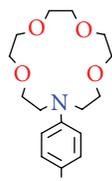
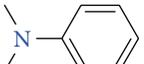
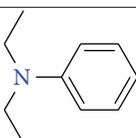
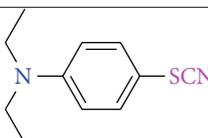
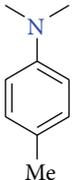
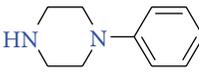
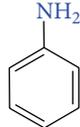
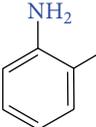
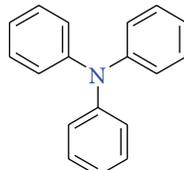
Entry	Substrate (a)	Product (b)	SESA (1 mol%)		Citric acid (10 mol%) [38]		m.p [found] m.p [lit.]
			Time (min)	Yield ^a %	Time (min) ^b Our time	Yield % ^b Our yield ^c	
1			2	97	20 40	91 90	68–70 72–73 [35]
2			10	96	20 40	82 80	77–79 79–81 [35]
3			3	98	7 15	88 78	92–95 97–99 [35]
4			—	—	—	—	—
5			10	98	25 45	85 83	130–132 125–127 [36]
6			2	98	—	—	79–81
7			8	97	60 80	65 45 ^d	90–92 74–76 [36]
8			40	78	45 70	83 79	66–68 66–69 [36]
9			35	81	40 65	79 74	80–82 77–80 [35]
10			40	96	60 100	79 73	75–80 82–84 [35]

TABLE 3: Continued.

Entry	Substrate (a)	Product (b)	SESA (1 mol%)		Citric acid (10 mol%) [38]		m.p [found] m.p [lit.]
			Time (min)	Yield ^a %	Time (min) ^b Our time	Yield % ^b Our yield ^c	
11			35	94	60 90	75 59	69–71 71–72 [35]
12							
13							
14							
15							
16							

^aIsolated yield.^bLiterature results.^cOur results for this experiment.^dOnly conversion is 45% for this entry.

As shown in Table 3, the substitution was highly regioselective, occurring at the *para*-position of the aromatic rings. In comparison with the previously reported method using other reagents, which requires refluxing conditions for some substrates, the assistance of ultrasonic irradiation, and a toxic solvent or oxidant, this method is suitable and has mild and green reaction conditions. In conclusion, we have developed an efficient, simple, and green-mediated thiocyanation of aromatic compounds with high regioselectivity. The described method has advantages such as a simple workup, a short reaction time, being metal free, using of mild reaction conditions, and a clean production of the desired products in high yields.

Herein, we wish to report the direct thiocyanation reaction catalyzed by SESA as a novel organocatalyst in water : ethanol.

In an initial experiment, the reaction between indole, hydrogen peroxide, and KSCN in water : ethanol was investigated. However, no reaction progress was detected after 12 hours without SESA (Table 1, entry 1). Then, we investigated the catalytic effect of phthalic acid on model reaction. Remarkably, the thiocyanation reaction catalyzed by 1 mol% of the SESA organocatalyst in water : ethanol (1 : 4) afforded the product an excellent yield of 97% and short reaction time (Table 1, entry 4 and Table 2, entry 8). The various molar ratios of reagents were used. A ratio of 1 : 3 : 3 (indole : KSCN : H₂O₂) was found to be the most suitable, and decreasing the amount of H₂O₂ or potassium thiocyanate increased the reaction time and lowered the yield (Table 1). A good range of aromatic and heteroaromatic compounds were selected for thiocyanation reaction with high regioselectivity and good yields being observed (Table 3). The reaction was mild and equally good for indoles and *N,N*-disubstituted anilines. As shown in Table 3, the substitution was highly regioselective occurring at the *para*-position of the aromatics

TABLE 4: Comparison of the thiocyanation of indole using the reported catalysts versus SESA.

Entry	System	Time (min)	Yield % [ref.]
1	SESA	10	97 [this work]
2	I ₂ /MeOH	50	85 [27]
3	DDQ/MeOH	50	94 [41]
4	DEAD/MeCN	45	85 [28]
	Mn(OAc) ₃ /HOAc	2 (h)	83 [11]
5	K10 clay/MeOH, 80°C	2 (h)	85 [26]
6	Citric acid/H ₂ O ₂ /H ₂ O	20	91 [35]

rings. However, in the case of a *N,N*,4-trimethylbenzenamine, orthothiocyanation did not occur (Table 3, entry 12) and 3-methylindole did not react (Table 3, entry 4). The proposed reaction mechanism is shown in [35].

In comparison with the previously reported method using other reagents which requires refluxing conditions for some substrates, the assistance of ultrasonic irradiation, toxic solvent or oxidant, this method works under milder and green reaction conditions (Table 4).

Ease of recycling of the catalyst is one of the most advantages of our method. When the reaction was complete, the product was extracted by chloroform and the residue was dried. Solvent was removed and recycled catalyst was reused in the next reaction. For the thiocyanation reaction, no significant loss of the product yield was observed when SESA catalyst was used after five times of recycling (Table 5).

4. Conclusions

In conclusion, we have shown that silica-supported SESA can be easily prepared from commercially available materials. This catalyst can be considered as a heterogeneous catalyst

TABLE 5: Recovery and Reusability of catalyst.

Number	Thiocyanation reaction	Yield %
1	First	97
2	Second	97
3	Third	94
4	Forth	93
5	Fifth	94

and efficiently affects the thiocyanation of a variety of organic compounds at room temperature. In comparison, SESA with citric acid as a trifunctional organocatalyst [35] showed that SESA is very effective. The time was reduced and yield was increased (Table 3). This procedure offers advantages such as simple workup, short reaction time, low cost of reagents, mild reaction conditions, recovery of catalyst, chemoselectivity, and clean formation of the desired products in high yields.

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