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Phthalic acid as a di-functional organocatalyst for the regioselective thiocyanation of aromatic compounds

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Abstract. A green and simple procedure for the thiocyanation of aromatic and heteroaromaric compounds in the presence of a catalytic amount of phthalic acid in water/ethanol is described. The reactions proceed at high yields, short reaction times and mild conditions.

1. Introduction

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 [1]. As for conventional catalysis with transitionmetal complexes, by using organic catalysts, large quantities of products are expected to be prepared using a minimal amount of small organic molecules [2,3]. The recent organocatalytic protocols are particularly attractive because of the mildness of the reaction conditions, operational simplicity, potential for development of large scale production, and the ready availability and low toxicity of the organocatalysts [4,5]. Organocatalyzed reactions using water as a solvent have attracted a great deal of attention, mainly because of low cost, 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 for today's synthetic community [6]. 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 [7]. For example, the thiocyanato group occurs as an important functionality in certain anticancer natural products formed by deglycosylation of glucosinolates derived from cruciferous vegetables [8-12]. 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 sulphide [11], aryl nitrile [12], thiocarbamate [13,14], and thionitrile [15]. Several methods have been developed for the thiocyanation of arenes using various reagents [16-18], such as nthiocyanatosuccinimide [19], Ceric Ammonium Nitrate (CAN) [20], acidic mont K10 clay [21], iodine/methanol [22], diethyl azodicarboxylate [23], IL-OPPh$_2$ [24], pentavalent iodine [25], IBX [26], FeCl$_3$ [27], potassium peroxydizulfate-copper(II) [28], SSA and SBSA [29],

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and HCl and H_5HO_6 [30]. However, most of the reported methods for the synthesis of aryl thiocyanates are associated with one or more of the following drawbacks; low yields, long reaction times, large amounts of catalyst, and use of toxic or expensive catalysts. Thus, the search for finding an efficient, inexpensive, and non-polluting method for the synthesis of this class of compounds is still of practical importance.

2. Experimental

2.1. General

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 was monitored by TLC using silica gel SIL G/UV 254 plates. The 1H NMR (300 MHz) and ^{13}C 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.

2.2. 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 phthalic acid (0.0083 g, 5 mol%) in H_2O (7-10 mL) was stirred at room temperature for 5 min. Then, H_2O_2 (%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 $CHCl_3$ (2 × 25 mL). Anhydrous Na_2SO_4 (3 g) was added to the organic layer and filtered off after 20 min. $CHCl_3$ was removed. The resulting product was purified by column chromatography on silica gel (Merck, 100-200 mesh, ethyl acetate-hexane, 1:9) to afford the pure thiocyanato derivative. We can use a similar procedure in thiocyanation reaction of aniline compounds. The yield was 0.159 g, (91%), mp 71-73°C. FT-IR (KBr): 2159, 3289, ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): δ ppm 8.87 (br s, 1H, NH), 7.83 (1H, d, J = 8.8 Hz), 7.46-7.23 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): 136.06, 131.22, 127.66, 123.83, 121.87, 118.65, 112.24, 91.76.

2.3. Selected specteral data

2.3.1. 3-Thiocyanatoindole (1b)

FT-IR (KBr). 2159 cm^{-1} (SCN), 3289 (NH). ^{1}H NMR ($CDCl_3$) d: 8.87 (br s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.46-7.23 (m, 4H). ^{13}C NMR ($CDCl_3$) d: 136.06, 131.2, 127.6, 123.8, 121.8, 118.6, 112.2, 91.7. MS (m/z)=174 (M^+). Anal. calcd for $C_9H_6N_2S$: C 62.05, H 3.47, N 16.08; found: C 62.25, H 3.34, N 16.15.

2.3.2. 1-Methyl-3-thiocyanatoindole (2b)

FT-IR (KBr): 2146 cm^{-1} (SCN). ^{1}H-NMR ($CDCl_3$) d: 7.84-7.36 (m, 5H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$) d: 137.1, 135.2, 128.4, 123.4, 121.6, 118.8, 112.1, 110.3, 33.4. MS (m/z)=188 (M^+). Anal. calcd for $C_{10}H_8N_2S$: C 63.80, H 4.28, N 14.88; found: C 64.01, H 4.15, N 14.92.

2.3.3. 2-Methyl-3-thiocyanatoindole (3b)

FT-IR (KBr): 2151 cm^{-1} (SCN), 3395 (NH), 3395. ^{1}H-NMR ($CDCl_3$ d): 8.55 (s, 1H), 7.71 (d, J = 6.9 Hz, 1H), 7.33-7.23 (m, 3H), 2.49 (s, 3H). ^{13}C NMR ($CDCl_3$) d: 142.1, 135.1, 128.6, 122.9, 121.5, 118.0, 111.3, 88.7, 12.0. MS (m/z) = 188 (M^+). Anal. Calcd for $C_{10}H_8N_2S$: C 63.80, H 4.28, N 14.88; found: C 63.65, H 4.41 N 14.80.

2.3.4. N1, N1, N8, N8-tetramethyl-4-thiocyanato naphthalene-1,8-diamine (6b)

FT-IR (KBr): 2055 cm^{-1} (SCN), ^{1}H NMR (FT-300 MHz, $CDCl_3$/TMS): δ ppm 7.97-7.66 (5H, m,), 3.37 (12H, s). ^{13}C NMR (75 MHz, $CDCl_3$): 148.23, 144.64, 135.14, 132.6, 129.36, 127.12, 121.38, 120.7, 118.04, 115.4, 111.30, 46.97. MS (m/z) = 271 (M^+). Anal. calcd for $C_{15}H_{17}N_3S$: C 66.39, H 6.31, N 15.48; found: C 66.53, H 6.28, N 15.59.

2.3.5. 4-Thiocyanato-N-phenylmorpholine (7b)

FT-IR (KBr): 2156 (SCN). ^{1}H NMR ($CDCl_3$) d: 7.48 (d, J = 8.29 Hz, 2H), 6.92 (d, J = 8.42 Hz, 2H), 3.88 (t, J = 4.69 Hz, 4H), 3.24-3.21 (t, J = 4.83 Hz, 4H). ^{13}C NMR ($CDCl_3$) d: 152.5, 133.7, 116.1, 111.9, 111.1, 67.1, 48.06. MS (m/z)=220 (M^+). Anal. calcd for $C_{11}H_{12}N_2OS$: C 59.97, H 5.49, N 12.72; found: C 59.79, H 5.65, N 12.85.

2.3.6. 4-Thiocyanato-N-phenyl-2,2-iminodiethanol (8b)

FT-IR (KBr): 2153, 3300. ^{1}H-NMR ($CDCl_3$) d: 7.43 (d, J = 6.5 Hz, 1H), 6.70 (d, J = 7.1 Hz, 2H), 3.75-3.60 (4H, m), 3.55-3.35 (m, 4H), 2.15 (s, 2H). ^{13}C-NMR ($CDCl_3$) d: 151.8, 132.1, 116.5, 114.3, 111.7, 58.7, 55.9. MS (m/z)=238 (M^+). Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C 55.44, H 5.92, N 11.76; found: C 55.66, H 5.79, N 11.85.

2.3.7. 4-Thiocyanato-N-phenyl-15-crown-5 (9b)

FT-IR (KBr): 2147 (SCN), 1094 (C-O), ^{1}H-NMR ($CDCl_3$) d: 7.35 (d, J = 5.5 Hz, 2H), 6.64 (d, J = 6 Hz, 2H), 3.57-3.72 (m, 20H). ^{13}C NMR ($CDCl_3$) d: 149.3, 134.7, 112.8, 105.9, 112.6, 71.2, 70.2, 69.9, 68.01, 52.6. MS (m/z)=352 (M^+). Anal. calcd for $C_{17}H_{24}N_2O_4S$: C 57.93, H 6.86, N 7.95; found: C 58.19, H 6.99, N 7.89.

2.3.8. 4-Thiocyanato-N,N-dimethylaniline (10b)

FT-IR (KBr): 2146 (SCN). ^{1}H-NMR ($CDCl_3$) d: 7.44 (d, J = 8.7, 2H), 6.69 (d, J = 8.7, 2H), 3.00 (s,

6H). ^{13}C NMR ($CDCl_3$) d: 151.6, 134.5, 113.1, 112.7, 106.3, 40.1. MS (m/z) = 178 (M^+). Anal. calcd for $C_9H_{10}N_2S$: C 60.64, H 5.65, N 15.72; found: C 60.45, H 5.84, N 15.65.

2.3.9. 4-Thiocyanato-N,N-diethylaniline (11b)
FT-IR (KBr): 2151 cm^{-1} (SCN). ^{1}H-NMR ($CDCl_3$) d: 7.5-7.34 (m, 2H), 7.2-7.13 (m, 1H), 6.63-6.61 (m, 1H), 3.37(q, J = 7.12 Hz, 4H), 1.146 (t, J = 5.4 Hz, 6H). ^{13}C NMR ($CDCl_3$) d: 149.1, 134.9, 125.2, 121.7, 112.6, 44.5, 12.3. MS (m/z) = 206 (M^+). Anal. calcd for $C_{11}H_{14}N_2S$: C 64.04, H 6.84, N 13.58; found: C 64.23, H 6.71, N 13.49.

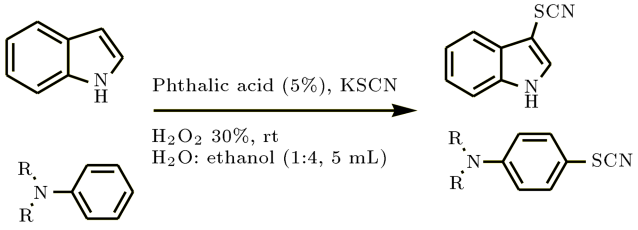
3. Results and discussion

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

In an initial experiment, we examined the reaction of indole in aqueous media in various ratios of H_2O_2 and KSCN. The results are summarized in Table 1. As Table 1 indicates, a ratio of 1:3:3 (indole: H_2O_2:KSCN) was found to be the most suitable in the presence of phthalic acid 5%. In the absence of catalyst, when indole was treated with hydrogen peroxide and KSCN, no product was obtained.

Table 1. Optimization amounts of phthalic acid, H_2O_2 and KSCN in water:ethanol(1:4, 5 mL).

Entry	Phthalic acid %	H_2O_2 (mmol)	KSCN (mmol)	Time (min)	Yeild %
1	—	3	3	12(h)	—
2	1	3	4	10(h)	54
3	3	3	3	1(h)	75
4	**5**	**3**	**3**	**10**	**91**
5	5	2	3	50	65
6	5	4	3	10	78
7	10	3	4	30	82
8	10	3	3	15	87
9	15	3	3	10	84
10	5	2	3	60	55
11	5	3	2	5(h)	60
12	5	—	—	24(h)	—



Scheme 1. Thiocyanation reaction of indole and N,N-disubstituted aniline in the presence of phthalic acid.

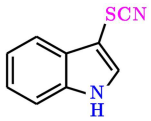
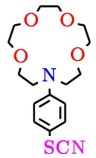
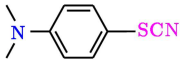
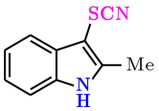
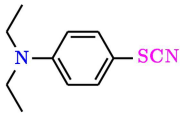
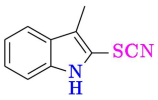
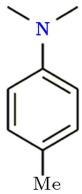
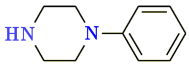
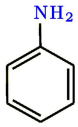
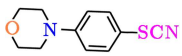
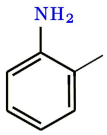
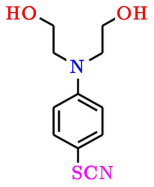
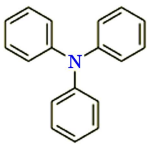
When the amount of catalyst was less than 5 mol%, the yield of product was reduced. Otherwise, increasing the catalyst loading from 5 to 15 mol% does not significantly change the yield. Also, the solvent effect was investigated using indole as a substrate. We carried out the reaction with the same concentration of reactants in H_2O, EtOH, MeOH, CH_3CN, CH_2Cl_2, THF, and AcOEt. Both the yields and the reaction times listed in Table 2 suggested that H_2O:ethanol (1:4) was the most favorable solvent for the thiocyanation in the presence of phthalic acid. Consequently, 5 mol% phthalic acid was used in subsequent experiments.

We then applied this reaction to a wide range of aromatic and heteroaromatic compounds (the results are summarized in Table 3). A good range of aromatic and heteroaromatic compounds underwent thiocyanation with high regioselectivities and excellent yields being observed in all cases. 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

Table 2. Optimization of solvent's ratios in presence of phthalic acid (5 mol%) in production of 3-thiocyanato-1H-indole **1b**.

Entry	Solvent	Time (min)	Yeild %
1	H_2O (5 mL)	120	85
2	ethanol (5 mL)	20	87
3	H_2O:ethanol(1:1, 5 mL)	35	79
4	H_2O:ethanol(1:1, 10 mL)	50	78
5	H_2O:ethanol(1:2, 5 mL)	40	81
6	H_2O:ethanol(1:3, 5 mL)	30	84
7	**H_2O:ethanol(1:4, 5 mL)**	**10**	**91**
8	H_2O:ethanol(1:5, 5 mL)	20	88
9	H_2O:ethanol(1:10, 5 mL)	20	87
10	E_2O:ethanol(2:1, 5 mL)	40	84
11	E_2O:ethanol(5:1, 5 mL)	70	81
12	MeCN	150	80
13	MeOH	60	83
14	CH_2Cl_2	150	45
14	THF	150	65
15	AcOEt	150	55

Table 3. Substrate scope in the thiocyanation reaction of arenes using KSCN/BSA/H_2O_2 under mild conditions.

Entry	Product (b)	Time (min)	m.p[found] m.p[lit.]	Yield %	Entry	Product (b)	Time (min)	m.p[found] m.p[lit.]	Yield %
1		10	68-70 72-73[29]	91	9		35	80-82 77-80[29]	81
2		15	77-79 79-81[29]	87	10		40	75-80 82-84[29]	98
3		30	92-95 97-99[29]	75	11		35	69-71 71-72[29]	85
4		—	—	—	12			No reaction	
5		60	130-132 125-127[30]	85	13			No reaction	
6		10	79-81	73	14			No reaction	
7		50	90-92 74-76[30]	87	15			No reaction	
8		40	66-68 66-69[30]	78	16			No reaction	

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 at high yield (Table 3, entries 6-11) but, *N*,*N*,4-trimethylaniline, 1-phenylpiperazine, aniline, o-toluidine and *N*,*N*,*N*-triphenylamine did not react with potassium thiocyanate and phthalic acid/H_2O_2 to afford the corresponding derivatives (Table 3, entries 13-16).

As shown in Table 3, the substitution was highly regioselective, occurring at the para-position of the aromatics rings. In comparison with the previously reported method using other reagents, which requires refluxing conditions for some substrates, with 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 simple work-up, short reaction time, is metal free, uses mild reaction conditions, and gives clean production of the desired products at high yields.

Herein, we wish to report the direct thiocyanation reaction catalyzed by phthalic acid as a organocatalyst in the presence of water:ethanol as a green solvent.

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 (Table 1). Then, we investigated the catalytic effect of phthalic acid in a model reaction. Remarkably, the thiocyanation reaction catalyzed by 5 mol% of the phthalic acid organocatalyst in the presence of water: ethanol(1:4) afforded the product at an excellent yield of 91%, with short reaction time (Table 1, entry 4 and Table 2, entry 6). Various molar ratios of reagents were used. A ratio of 1:3:3 (indole:KSCN:H_2O_2) was found to be the most suitable, and decreasing the amount of H_2O_2 or potassium thiocyanate increased the reaction time and lowered the yield (Table 1). A good range of aromatic and heteroaromatic compounds were selected to the 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 rings. However, in the case of a *N*,*N*,4-trimethylbenzenamine, ortho thiocyanation did not occur (Table 3, entry 12) and 3-methylindole was not reacted (Table 3, entry 4). The proposed reaction mechanism is shown in [29].

In comparison with the previously reported method (Table 4), using other reagents that require refluxing conditions for some substrates, and the assistance of ultrasonic irradiation, toxic solvent or oxidant, this method works under milder and green reaction conditions. In conclusion, water:ethanol as solvent, short reaction times, low cost reagents, high yields, and mild and green reaction conditions are major advantages of the described methodologies.

Table 4. Comparison of the previously reported method for synthesis of 3-Thiocyanatoindole.

Number	Oxidant/Catalyst/ Condition	Time/ Yield%	[ref.]
1	$Mn(OAc)_3$/HOAc/rt	.../83	6
2	Oxone/MeOH/rt	43 min/88	18
3	K10 clay, 80°C,	2 h/85	21
4	I_2/MeOH	50 min/85	22
5	$FeCl_3/CH_2Cl_2$/rt	3.5 h/86	27
6	H_2O_2/Phtalic acid/H_2O:EtOH/rt	10 min/91	This work

4. Conclusions

In continuation of our study in regioselective thiocyanation reaction [29,30], we have developed an efficient, simple and green thiocyanation of aromatic and heteroaromatic compounds using phthalic acid/H_2O_2/KSCN in water:ethanol as solvent, which takes place with high regioselectivity. This procedure offers advantages such as simple work-up, short reaction time, low cost of reagents, mild reaction conditions and clean formation of the desired products in high yields.

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