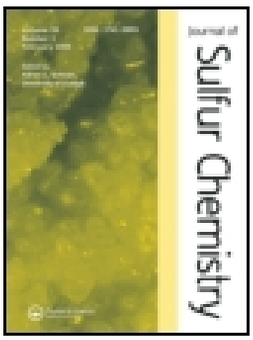

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Oxidant-free thiocyanation of phenols and carbonyl compounds under solvent-free conditions by $AlCl_3/NH_4SCN$

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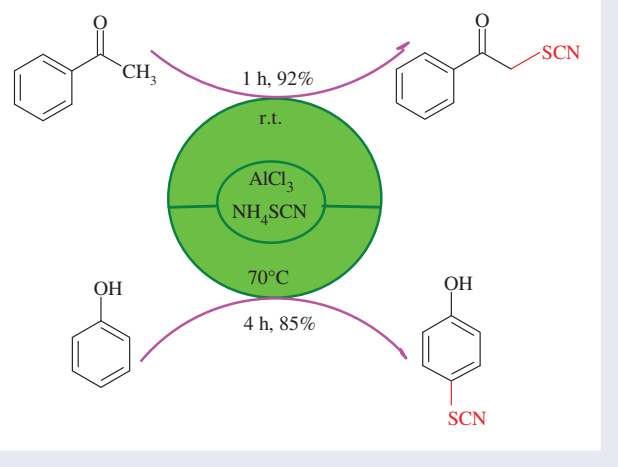
ABSTRACT

A simple, efficient, solvent-free, and mild method for thiocyanation of phenols by ammonium thiocyanate (NH_4SCN) in the presence of $AlCl_3$ has been developed. This new methodology was used to prepare para-thiocyanated products in good to excellent yields at 70°C. In addition, the successful α-thiocyanation of various ketones has also been described. Finally, a plausible mechanism of thiocyanation has been suggested.



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Thiocyanation; phenol; carbonyl compound; $AlCl_3$; solvent-free conditions

1. Introduction

Thiocyanate is a versatile synthon,[1] which can be easily transferred to other functional groups such as sulfides,[2] thioesters,[3] mercaptoindoles,[4] and thiocarbamates.[5] In particular, α-ketothiocyanates are useful intermediates in the synthesis of sulfur-containing heterocycles, such as thiazoles.[6] Some of these thiazoles exhibit herbicidal and other important biological properties.[7] Thiocyanation of aromatic and heteroaromatic compounds is an important transformation in both organic synthesis and in the production of pharmaceuticals.[8,9] Organic compounds that contain the thiocyano group have been used as precursors for agrochemical, dyes, and drugs.[10] This moiety is a significant

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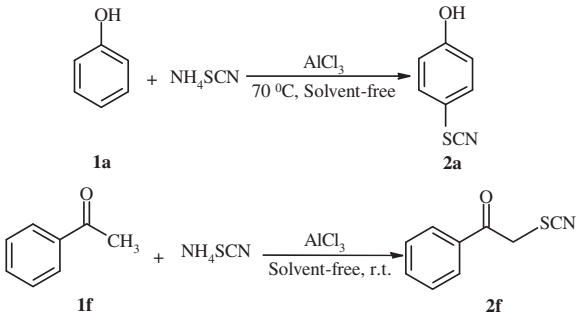


Scheme 1. Thiocyanation of phenols and carbonyl compounds.

functionality in several anticancer agents.[11] Several methods for the α-thiocyanation of carbonyl compounds and phenols using various reagents such bromo dimethylsulfonium bromide/ammonium thiocyanate,[12] (dichloroiodo)benzene and potassium thiocyanate,[13] heteopolyacid/ammonium thiocyanate,[14] (dichloroiodo)benzene/lead (II) thiocyanate,[15] potassium peroxydisulfate/copper (II) complex,[16] I_2 /ammonium thiocyanate,[17] NH_4VO_3/$KHSO_4$/ammonium thiocyanate,[18] and bromodimethylsolfonium bromide/ammonium thiocyanate[19] have been reported. However, most of these reported methods involve the use of a large excess of strong oxidizing agents and toxic metal thiocyanates. Since organosulfur compounds have become increasingly useful and important in the field of drugs and pharmaceuticals,[20] the development of simple, convenient, and efficient approaches for their synthesis is desirable.

Anhydrous $AlCl_3$ is probably the most commonly used Lewis acid. This white relatively nontoxic powder with LD50 = 3730 mg kg^{-1} is a potent moisture-adsorbent. Water removal can be achieved by sublimation to produce anhydrous $AlCl_3$. It has been extensively used as a strong Lewis acid in many organic reactions such as Friedel-Crafts reactions and Fries rearrangement.[21,22] Recently, $AlCl_3$ has been employed for some other transformations such as generation of highly strained cycloheptadienones,[23] selective synthesis of 2-aryl-2*H*- and 4-aryl-4*H*-3,5-diformylpyrans,[24] asymmetric aldehydes arylation,[25] 1,4-dihydropyridines synthesis,[26] aldol cyclocondensation,[27] 1,2,3,4-tetrahydroquinolines synthesis,[28] and substituted guanidines synthesis.[29]

In a continuation of our research interest on thiocyanation of organic compounds, [30–34] and following our successful results in thiocyanation of *N*-containing compounds, [35] herein we report $AlCl_3$ as a commercially available and low-cost promoter for the thiocyanation of some phenols and ketones in the presence of NH_4SCN, as thiocyanate ion source, under solvent-free conditions (Scheme 1).

2. Results and discussion

Thiocyanation of phenols were performed in the presence of $AlCl_3$, at 70°C under solvent-free conditions. Initial studies were done using phenol as a substrate model. The results are summarized in Table 1. By checking various amounts of NH_4SCN and $AlCl_3$, we determined that a NH_4SCN/$AlCl_3$ molar ratio (2/1) afforded the best results (Entries 1–4). We also optimized the temperature and confirmed that 70°C is the most effective (Entries

Table 1. Optimization of the reaction conditions for the synthesis of 4-thiocyanatophenol **1a**.

Entry	Condition[a]	Temp. (°C)	Time (h)	Yield[b] (%)
1	$AlCl_3/NH_4SCN$ molar ratio (0.5/2)/solvent-free	r.t.	1.5	80
2	$AlCl_3/NH_4SCN$ molar ratio (1/2)/solvent-free	r.t.	0.5	85
3	$AlCl_3/NH_4SCN$ molar ratio (1.5/2)/solvent-free	r.t.	0.75	80
4	$AlCl_3/NH_4SCN$ molar ratio (2/2)/solvent-free	r.t.	1	75
5	$AlCl_3/NH_4SCN$ molar ratio (1/2)/solvent-free	40	2	65
6	$AlCl_3/NH_4SCN$ molar ratio (1/2)/solvent-free	60	2	70
7	$AlCl_3/NH_4SCN$ molar ratio (1/2)/solvent-free	70	1	92
8	$AlCl_3/NH_4SCN$ molar ratio (1/2)/MeOH[c]	r.t.	2.5	45
9	$AlCl_3/NH_4SCN$ molar ratio (1/2)/EtOH[c]	r.t.	4	70
10	$AlCl_3/NH_4SCN$ molar ratio (1/2)/CH_3CN[c]	r.t.	2	50

[a]1 mmol of phenol was used.
[b]Isolated yields.
[c]5 mL of solvent was used.

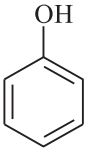
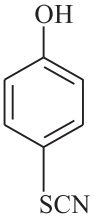
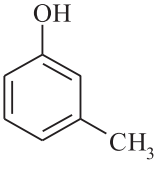
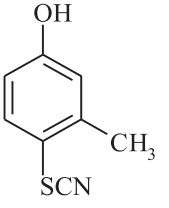
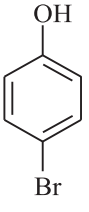
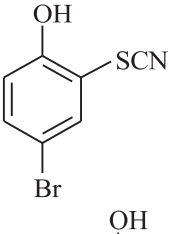
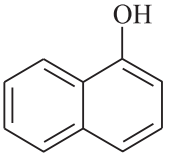
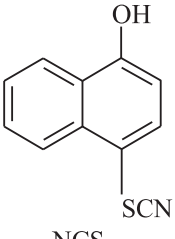
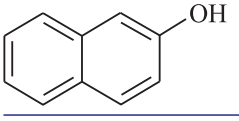
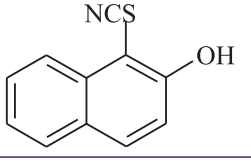
5–7). The effect of solvent has also been examined (Entries 8–10). The data confirmed that solvent-free conditions gave the best results.

Therefore, the reactions were performed with these experimentally determined optimized conditions using 1 mmol of substrate, 1 mmol of $AlCl_3$, and 2 mmol of NH_4SCN at 70°C under solvent-free conditions. According to the data in Table 2, phenol **1a** and its electron-donating derivative 3-methyl phenol **1b** successfully thiocyanated at their 4-positions. 4-Bromo phenol **1c** with an electron-withdrawing substituent yielded its corresponding 4-bromo-2-thiocyanatophenol **2c**. On the other hand, 4-bromophenol is blocked at the para-position, so the thiocyanation occurred at C_2 of the phenol ring. 1-Naphthol **1d** and 2-naphthol **1e**, as other samples of phenolic group, produced 4-thiocyanato-1-naphthol **2d** and 1-thiocyanato-2-naphthol **2e**, respectively. For the case of 2-naphthol **1e**, oxathiole has previously been reported as the main product instead of **2e**.[13]

We have also examined and successfully achieved α-thiocyanation of some carbonyl compounds in the presence of $AlCl_3$, at room temperature under solvent-free conditions. Initially, acetophenone **1f** has been chosen as the model substrate for this study. α-Thiocyanation has been performed at various molar ratios of $AlCl_3/NH_4SCN$ at room temperature under solvent-free conditions (Table 3, Entries 1–4). The optimal $AlCl_3/NH_4SCN$ ratio was determined to be 2/1 (Entry 2). Increasing the temperature did not enhance the reaction progress (Entries 5,6). In addition, performing the reaction in the presence of different solvents did not improve the thiocyanation (Entries 7–9). The result presented in Table 3 confirms that doing the thiocyanaion reactions under these optimized conditions using a 1/2 molar ratio of $AlCl_3/NH_4SCN$ at room temperature without a solvent is the most appropriate reaction protocol.

Thiocyanation of **1f** occurred at the α-position of the carbonyl moiety using these optimized conditions to afford the 1-phenyl-2-thiocyanatoethanone **2f** within 4 h in 85% yield (Scheme 1). Similarly, other substituted acetophenones, such as 2-hydroxy-, 4-nitro-, 4-methoxy-, and 4-bromo derivatives **1g–1j** underwent smooth thiocyanation to furnish their corresponding α-thiocyanoketones **2g–2j** in good yields (Table 4). The excellent reactivity of $AlCl_3$ in the thiocyanation of different aryl methyl ketones prompted us to extend this method to 4-methyl cyclohexanone **1k** as a representative cyclic ketone. This compound gave the corresponding 2-thiocyano-4-methylcyclohexanone **2k** in excellent yield.

Table 2. Thiocyanation of phenols **1a–1e** with NH_4SCN (2 mmol) in the presence of $AlCl_3$ (1 mmol) under solvent-free conditions and at 70°C.

Substrate		Product[a]		Time (h)	Yield[b] (%)	m.p.[c] (°C)
	**1a**		**2a**	1	92	52–53, Lit. [19]: 51–52
	**1b**		**2b**	0.5	80	122–125
	**1c**		**2c**	1.5	83	133–135
	**1d**		**2d**	1	68	146–147, Lit. [36]: 147–148
	**1e**		**2e**	1	45	104, Lit. [37]: 107

[a]All products were characterized by comparison of their spectroscopic data (IR, ^{1}H-NMR, and CHN analysis) with those reported in literature.
[b]Yield of isolated product.
[c]Reference of known compounds.

Although the actual mechanism of the thiocyanation is not obvious, we suggested a plausible route in Scheme 2. Anhydrous $AlCl_3$, as Lewis acid, could form a complex **A** with NH_4SCN. Nucleophilic attack of phenol **1a** on **A** produces **B**, which is followed by a proton-release leading to the corresponding thiocyanated product **2a**.

3. Conclusion

In conclusion, we report $AlCl_3$ as a commercially available, inexpensive, and non-volatile promoter for the thiocyanation of various phenols and carbonyl compounds. This

Table 3. Screening the reaction conditions for the synthesis of α-thiocyanatoacetophenone **1f**.

Entry	Condition[a]	Temp. (°C)	Time (h)	Yield[b] (%)
1	$AlCl_3/NH_4SCN$ molar ratio (0.5/2)/solvent-free	r.t.	1.25	75
2	$AlCl_3/NH_4SCN$ molar ratio (1/2)/solvent-free	r.t.	4	85
3	$AlCl_3/NH_4SCN$ molar ratio (1.5/2)/solvent-free	r.t.	5.5	45
4	$AlCl_3/NH_4SCN$ molar ratio (2/2)/solvent-free	r.t.	4.5	60
5	$AlCl_3/NH_4SCN$ molar ratio (1/2)/solvent-free	50	2.5	50
6	$AlCl_3/NH_4SCN$ molar ratio (1/2)/solvent-free	70	3	65
7	$AlCl_3/NH_4SCN$ molar ratio (1/2)/MeOH[c]	r.t.	3.25	70
8	$AlCl_3/NH_4SCN$ molar ratio (1/2)/EtOH[c]	r.t.	5	54
9	$AlCl_3/NH_4SCN$ molar ratio (1/2)/CH_3CN[c]	r.t.	7	-

[a]1 mmol of acetophenone was used.
[b]Isolated yields.
[c]5 mL of solvent was used.

non-corrosive and commonly found Lewis acid promotes the activation of NH_4SCN for the nucleophilic attack of the substrates. The regioselectivity of the procedure was specified in para-thiocyanation of phenols and α-thiocyanation of carbonyl compounds. In addition, the absence of hazardous oxidants and non-green solvents, easy work-up, and its wide-range thiocyanating power for different substrates are some noteworthy advantages of the reported procedure.

4. Experimental section

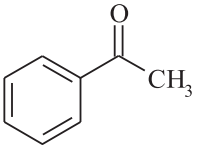
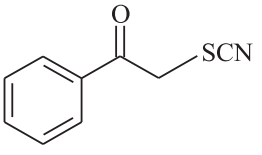
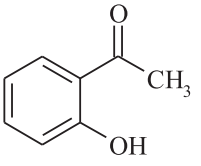
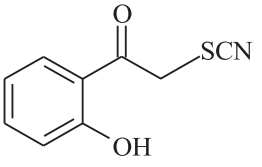
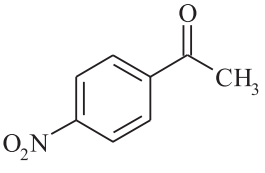
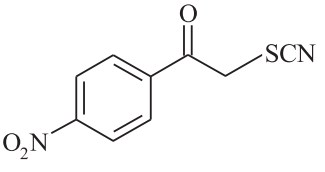
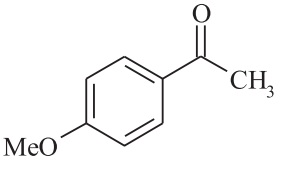
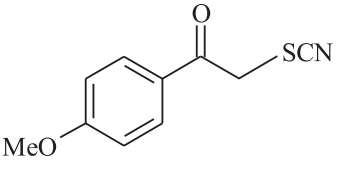
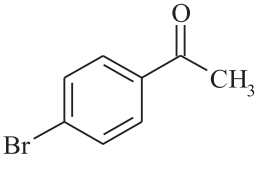
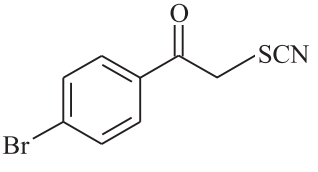
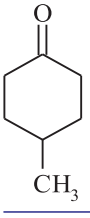
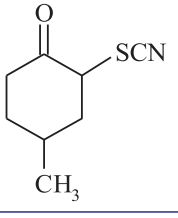
4.1. General

Chemicals and solvents were purchased from Merck, Aldrich, and Alfa Aesar and used without further purifications. Commercial $AlCl_3$ was heated and its sublimated anhydrous form was used. Melting points were determined using a Stuart Scientific apparatus and are uncorrected. All products were identified by their spectral data. IR spectra (KBr discs, 500–4000 cm^{-1}) were recorded using a Bruker FT-IR model Tensor 27 spectrometer. ^{1}H-NMR spectra were recorded in $CDCl_3$ solvent on a Brucker 400 MHz spectrometer. Elemental analyses were determined using a Thermo-Finnigan Flash EA 1112 Series. Preparative layer chromatography (PLC) was carried out on 20×20 cm^2 plates, coated with a 1 mm layer of Merck silica gel PF_{254}, prepared by applying the silica as slurry and drying in air. Yields refer to isolated products.

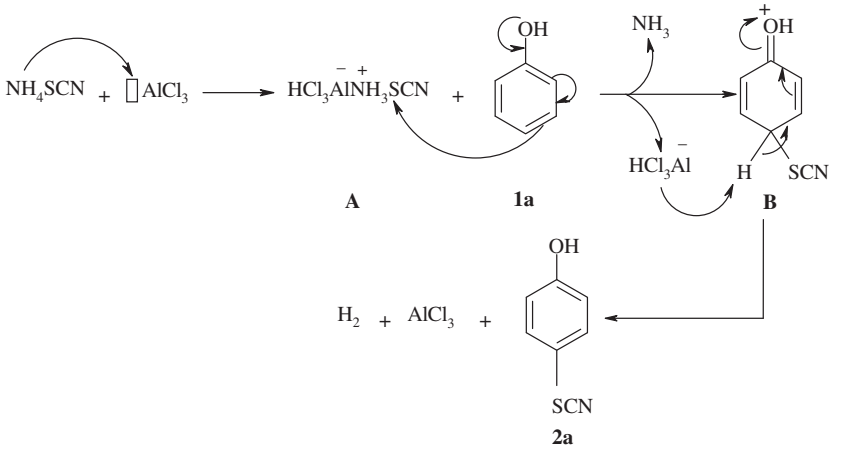
4.2. General procedure for thiocyanation

A mixture of substrates **1a–1e** (1 mmol), anhydrous $AlCl_3$ (1 mmol), and NH_4SCN (2 mmol) was stirred at 70°C. The progress of the reaction was monitored by TLC (eluent: *n*-hexane:EtOAc, 3:1). After completion (Table 2, 0.5–1.5 h), the residue was diluted with distillated water (20 mL) and extracted with chloroform (2×20 mL). The combined organic layer was dried over $MgSO_4$ and evaporated. The resulting crude product was purified by plate chromatography on silica gel (PLC) to afford the pure products **2a–2e** (45–92%). In the case of carbonyl compounds, a mixture of substrates ***1f–k*** (1 mmol), anhydrous $AlCl_3$ (1 mmol), and NH_4SCN (2 mmol) was stirred at room temperature for the appropriate time (Table 4, 1–5 h). The work-up procedure is the same as that of phenols. The pure products were obtained in 68–85%. All the products were characterized by

Table 4. α-Thiocyanation of carbonyl compounds **1f–1k** with NH_4SCN (2 mmol) in the presence of $AlCl_3$ (1 mmol) under solvent-free conditions at room temperature.

Substrate		Product[a]		Time (h)	Yield[b] (%)	m.p.[c] (°C)
	**1f**		**2f**	4	85	69–70, Lit. [38]: 68–70
	**1g**		**2g**	3.5	70	112–114
	**1h**		**2h**	5	70	118–120, Lit. [12]: 119–120
	**1i**		**2i**	4	68	120–122, Lit. [12]: 121–125
	**1j**		**2j**	4.5	73	123–125, Lit. [39]: 122–125
	**1k**		**2k**	1	82	Semi solid

[a]All products were characterized by comparison of their spectroscopic data (IR, ^{1}H-NMR) with those reported in literature.
[b]Yield of isolated product.
[c]Reference of known compounds.



Scheme 2. The proposed mechanism of thiocyanation by $AlCl_3/NH_4SCN$.

comparison of their spectroscopic data (FT-IR, ^{1}HNMR, and CHN analysis) with those of the authentic samples in literature. The spectral data of new compounds are given below.

4-Thiocyanato-3-methylphenol (**2b**): FT-IR (KBr): ν = 3423 (OH), 2220 (SCN), 1547, 1420, 1098, 656 (C-S) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.72 (s, 3H, CH_3), 5.22 (s, 1H), 6.43-(s, 1H, OH), 7.23–6.91 (m, 2H) ppm. Anal. Calcd for C_8H_7SNO: C 59.37%, H 7.27%, N 9.68%. Found: C 59.25%, H 7.95%, N 9.75%.

4-Bromo-2-thiocyanatophenol (**2c**): FT-IR (KBr): ν = 3421 (OH), 2256 (SCN), 1461, 1241, 825 (C–S) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 6.43 (s, 1H, OH), 6.75–6.84 (m, 2H), 6.89–6.92 (m, 1H) ppm. Anal Calcd. for C_7H_4SNOBr: C 36.54%, H 1.75%, N 6.95%. Found: C 37.01%, H 1.83%, N 7.21%.

α-Thiocyanato-2-hydroxyacetephenone (**2g**): FT-IR (KBr): ν = 3428 (OH), 2177 (SCN), 1728(C=O), 1644, 1458, 1108, 790 (C–S) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.57 (s, 2H), 6.91–7.12 (m, 2H), 7.13–7.20 (m, 2H), 7.61 (s, 1H, OH) ppm. Anal. Calcd for $C_9H_7SNO_2$: C 55.95%, H 3.65%, N 7.25%. Found: C 55.01%, H 3.78%, N 7.78%.

α-Thiocyanato-4-methylcyclohexanone (**2k**): FT-IR (KBr): ν = 2068 (SCN), 1634 (C=O), 1416, 1104, 794, 671 (C–S) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.49 (s, 3H, CH_3), 1.49–1.99 (m, 2H), 1.33–1.45 (m, 1H), 1.14–1.30 (m, 5H) ppm. Anal. Calcd for $C_8H_{11}SNO$: C 56.77%, H 6.55%, N 9.45%. Found: C 56.93%, H 6.41%, N 9.24%.

Disclosure statement

No potential conflict of interest was reported by the authors.

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