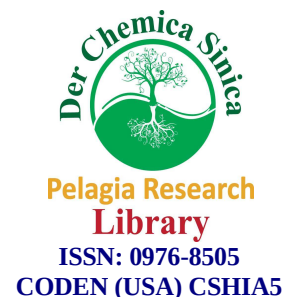




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Simple, efficient and green thiocyanation of aldehydes using ionic liquid

Sangita Makone* and Chanda Gawande

Research Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Vishnupuri,
Nanded-431606 India

ABSTRACT

A green method for thiocyanation of aldehydes using ionic liquid as a catalyst, provide environmental friendly and simple protocol for thiocyanated aldehydes as major outcome in short reaction time.

Keywords: Thiocyanation, Aldehydes, Ionic Liquid, NH_4SCN

INTRODUCTION

An electrophilic thiocyanation of aromatics is an important carbon-heteroatom bond formation reaction, thiocyanates are the versatile synthons in organic synthesis[1-4]. It is innovative and fast methods for synthesis of thiocyanate group containing aromatic systems. In view of the versatility of thiocyanate group, it will be important to probe this. Several methods have been developed for the thiocyanation of arenes by using various reagents under certain conditions[5-7]. But only a limited ceric ammonium nitrate[8], Iodine/methanol[9], IL- OPPh_2 [10], potassium peroxydisulfate and $\text{HCl}/\text{H}_2\text{O}_2$ [11], Iodine/ammonium thiocyanate [12], ferric chloride/ammonium thiocyanate[13], and oxone/ammonium thiocyanate[14]. Very recently, 2,3-dichloro-5,6-dicyano benzoquinone (DDQ)/ NH_4SCN [15], $\text{HIO}_3/\text{NH}_4\text{SCN}$ [16] and p-toluene sulfonic Acid/ NH_4SCN [17] have been applied to the thiocyanation of aromatic systems. All these methodologies having some lacunae such as the little availability or tough preparation of starting materials, the necessity of large amount of strong oxidizing reagents, minimum yields for some compounds, and performed in certain harsh conditions [18-22]. Hence, requirement for build up alternative synthesis path accessible to the thiocyanation is in high insist [23-27]. Increasing attention in the make use of environmentally benign reagents and procedures, aqueous mediated reactions have got considerable notice in this, because of environmentally safety reasons. Water is universal solvent for chemical reactions because it has high dielectric constant and high cohesive energy density as compared to other organic solvents. It has also special effect due to which it shows novel solvation and assembly processes and it is nontoxic, ecofriendly behaviour, readily available, and cheapest compared to expensive hazardous solvents [28]. The growth of an efficient and suitable thiocyanation synthetic methodology in aqueous medium is an significant research area [29-30]. Thiocyanated aromatic aldehydes can shows antimicrobial[31], antiinflammatory[32], antipyretic and analgesic[33] activity. Herein we develop simple and efficient path for the thiocyanation of aromatic aldehydes using ionic liquid.

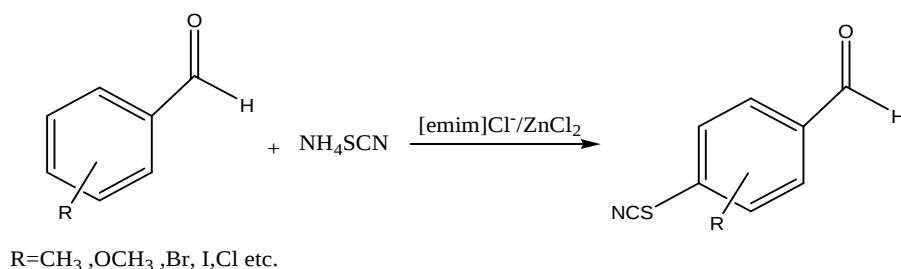
MATERIALS AND METHODS

IR spectra were recorded on a Shimadzu FTIR. ^1H NMR spectra were recorded in DMSO- d_6 at 400 MHz using TMS as an internal standard. Mass spectra were recorded on Shimadzu GC-MS using ionization technique. The elemental analysis was carried out on Flash EA-1112, 50/60 Hz, CHNS analyzer. The progress of the reactions was monitored by

TLC. All the chemicals were purchased from Avra, spectrochem, Alfa aesar chemicals. All melting points were measured on Veego digital melting point apparatus .

GENERAL PROCEDURE

To a mixture of aromatic aldehyde (1mmol) and ammonium thiocyanate (2mmol) and 1-ethyl-3-methyl imidazolium chloride/ZnCl₂ (0.85 ml) was added. The mixture was stirred at room temperature for appropriate time. Progress of reaction was monitored by TLC. The product formed was recrystallised using ethanol.



RESULTS AND DISCUSSION

It is observed that thiocyanation investigated at various conditions. In the absence of ionic liquid, reaction was not accomplished, but in the presence of very small amount of it, the reaction progresses with best results. Ionic liquid is efficiently acting as a catalyst towards the thiocyanation of aromatic aldehydes. The ionic liquid was recovered by distillation and reused for three times.

Table 1.1: Effect of reagent on thiocyanation of aromatic aldehydes

Reagent Used	Time (hr:min)	Yield (%)
1) NaSCN	04:40	75
2) KSCN	04:05	90
3) Mg(SCN) ₂	03:32	77
4) NH ₄ SCN	02:45	94

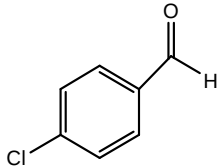
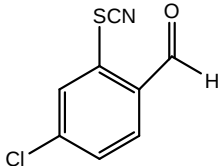
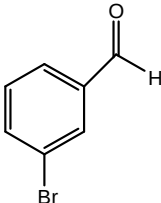
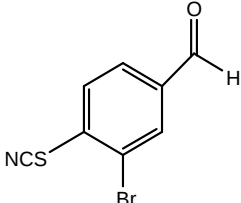
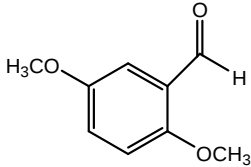
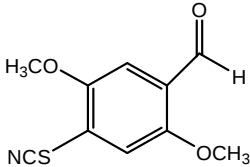
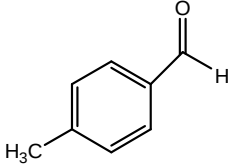
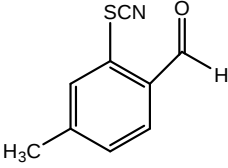
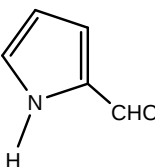
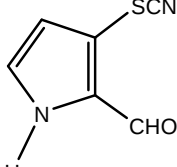
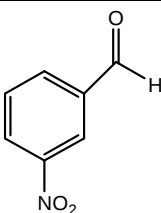
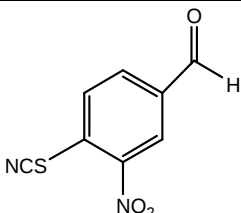
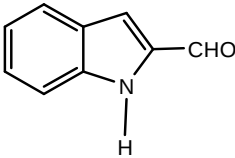
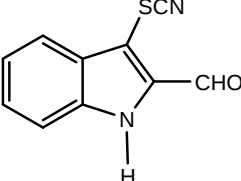
Table 1.2: Recycling effect of ionic liquid on thiocyanation of aldehydes

Ionic Liquid Reuse	Yield (%)
1) I st	97
2) II nd	94
3) III rd	89

Table 1.3: Solvent effect on thiocyanation of aromatic aldehydes

Solvent	Time(hr:min.)	Yield (%)
1) Carbon tetra chloride	10:00	77
2) Dichloro methane	08:00	67
3) Acetonitrile	07:00	75
4) Tetrahydrofuran	06:35	69
5) Ethanol	00:40	77
6) Water	00:21	91
7) Ionic Liquid	00:19	96

Table 2: Thiocyanation of aromatic aldehydes using ionic liquid

Sr. No.	Substrate	Product	Reaction Time (min.)	Yield (%)	M.P. (°C)
a			52	78	241
b			54	81	179
c			34	75	168
d			38	82	187
e			30	85	146
f			55	74	188
g			32	87	192

h			40	70	189
i			42	76	163
j			45	74	177
k			30	83	169
l			35	80	156

SPECTRAL DATA**2b) 3-Bromo 4-thiocyanato benzaldehyde :-**Solid; IR (KBr) : 2924,2150,1712,608 m/e : 244.1(m⁺), 242.8(m⁺), 241.3, 114.4¹H NMR : (CDCl₃) 7.24 (d, 1H), 7.55 (d, 1H), 7.82 (d, 1H), 9.86 (s, 1H)¹³CNMR : (CDCl₃) 124.2,130.4,132.9,142.0,192.1Elemental Analysis For : C₈H₄BrNOS

C,39.60;H,1.76;Br,32.85;N,5.85;O,6.54;S,13.40

2d) 4-methyl 2-thiocyanato benzaldehyde :-Solid; IR (KBr) : 3020, 2149,1715, 590 m/e : 177.4(m⁺), 162.2, 119.1¹H NMR : (CDCl₃) 2.32(s,3H), 7.15(d, 1H), 7.05 (t, 1H), 7.55 (t, 1H), 10.18 (s, 1H)¹³CNMR : (CDCl₃) 24.5,111.2,125.4,129.1,131.4,132.2,145.9,190.8Elemental Analysis For : C₉H₇NOS

C,60.90;H,4.07; N,7.95;O,8.99;S,18.09

2g) 3-thiocynato-1-H-indole-2-carbaldehyde :-Solid; IR (KBr) :3029,2150,1695,792 m/e :202.3(m⁺), 174.4, 143.8¹HNMR:(CDCl₃) 7.12(q,1H),7.23(q,1H),7.35(t,1H),7.71(t,1H),

9.59(s,1H),10.15(s,1H)

¹³CNMR : (CDCl₃) 111.2,115.9,120.8,132.4,144.7,180.2Elemental Analysis For : C₁₀H₆N₂OS

C,58.40;H,2.75;N,14.05;O,8.41;S,16.39

2l) 4-hydroxy-2-thiocyanato benzaldehyde :-

Solid; IR (KBr) : 3121,2140,1705,801 m/e : 179.1(m⁺), 181.1,121.4

¹H NMR : (CDCl₃) 6.69(t,1H), 6.79(d,1H), 7.36 (t, 1H) , 10.19 (s,1H),4.9(s,1H)

¹³CNMR : (CDCl₃) 111.5,118.2,118.7,123.3,127.3,130.5,165.3,190.1

Elemental Analysis For : C₈H₅NO₂S

C,54.12;H,2.85; N,7.62;O,18.06;S,17.35

CONCLUSION

In short a suitable, simple, strategy has been developed by using simple techniques for green thiocyanation of aromatic aldehydes using Ionic Liquid .This practice offers many advantages such as short reaction time, simple workup , mild reaction conditions, reuse of catalyst. catalyst can be recycled and reused for three times.

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