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Green Thiocyanation of Aryl Aldehydes Using Ethyl Methyl Imidazolium Chloride

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ABSTRACT

A green method for thiocyanation of aldehydes using 1-ethyl-3-methyl imidazolium chloride ionic liquid as a catalyst, provide environmental friendly and simple protocol for thiocyanated aldehydes as major outcome in short reaction time. Different substituted thiocyanated aldehydes are the sole outcomes of this method. These thiocyanato aldehydes are useful intermediates in the synthesis of heterocycles bearing sulfur, in which the thiocyanate group will be readily altered into other sulfur-containing compounds.

Keywords: Emim[Cl],Aldehydes, Ammonium thiocyanate, RT (Room Temperature)

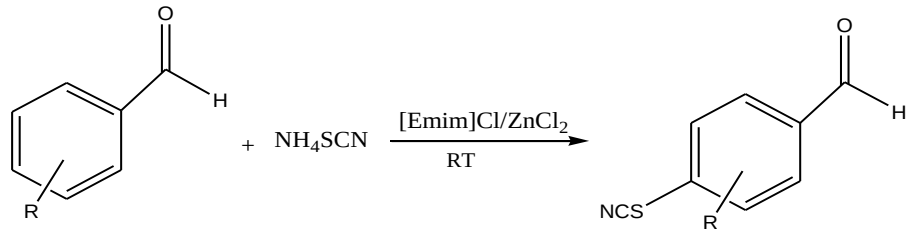
I. INTRODUCTION

An electrophilic thiocyanation of aromatic compunds is significant carbon-heteroatom bond formation reaction, thiocyanates are the versatile synthons in organic synthesis. [10-13] It is innovative and fast methods for synthesis of thiocyanate group containing aromatic systems. In view of the adaptability of thiocyanate group, it will be important to explore this. A number of strategies have been created for the thiocyanation of arenes using different reagents under optimum conditions. [14-16] But only a limited ceric ammonium nitrate [17], Iodine/methanol [18],IL-$OPPh_2$ [19], potassium peroxydisulfate and HCl/H_2O_2 [20], Iodine/ammonium thiocyanate [21], ferric chloride/ammonium thiocyanate [22],and oxone/ammonium thiocyanate. [23] Very recently, 2,3-dichloro-5,6-dicyano benzoquinone (DDQ/NH_4SCN [24], HIO_3/NH_4SCN [25] and p-toluene sulfonic Acid/NH_4SCN [26] have been applied to the thiocyanation of aromatic systems. All these methodologies having some lacunae such as the little availability or tough preparation of substrate, the need of large amount of strong oxidizing reagents, least yields for some compounds, and performed in certain harsh conditions. [27-31] Hence, requirement for build up alternative synthesis path accessible to the thiocyanation is in high insist. [32-36] Increasing attention in the make use of environmentally friendly procedures and reagents, aqueous mediated reactions have gained considerable notice in this, because of environmentally safety reasons. Due to the high dielectric constant and high cohesive energy density water is universal solvent for chemical reactions as compared to other organic solvents. It has also special effect due to which it shows novel solvation and assembly processes and it is ecofriendly, nontoxic, easily available, and inexpensive

compared to costly hazardous solvents. [37] The growth of an proficient and appropriate thiocyanation imitation methodology in water is an significant research area. [38-39] Thiocyanated aromatic aldehydes can shows antimicrobial [40], anti-inflammatory [41], antipyretic and analgesic [42] activity. Herein we designed simple and efficient route for the thiocyanation of aromatic aldehydes using ionic liquid.

II. PRESENT WORK

Here in we have reported simple, efficient and green method for thiocyanation of substituted benzaldehyde using ammonium thiocyanate as reagent under infiuence of ethyl methyl imidazolium chloride and zinc chloride as catalyst. This RTIL is acts as good catalyst to yield more product in short reaction time and easy work up.



$R=CH_3$,OCH_3 ,Br, I,Cl

Scheme: green thiocyanation of aryl aldehydes using RTIL

III. EXPERIMENTAL SECTION

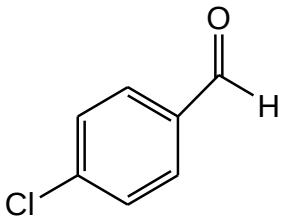
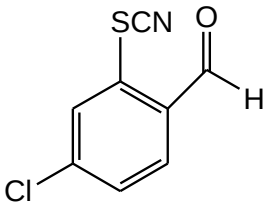
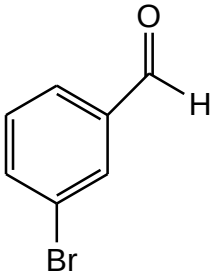
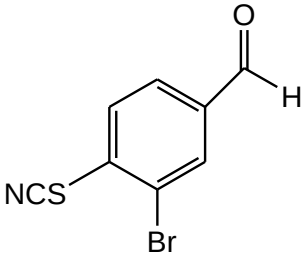
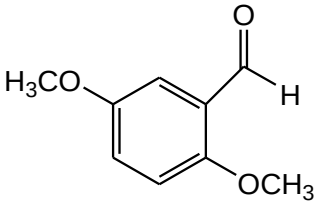
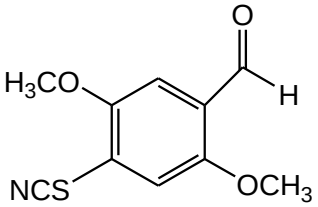
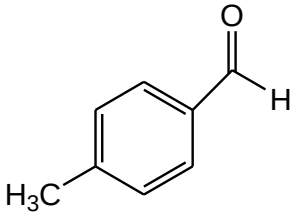
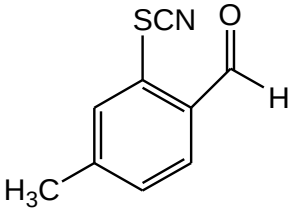
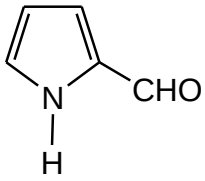
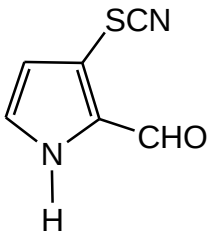
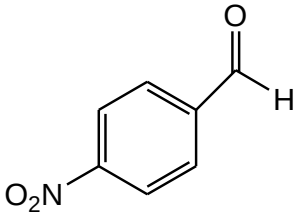
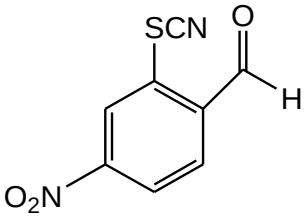
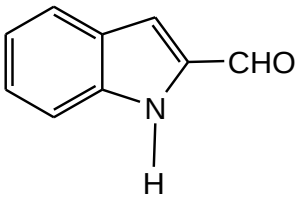
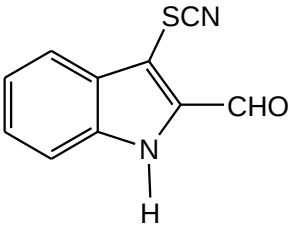
IR spectra were measured on a shimadzu FTIR,^{1}H NMR spectra were recorded using $CDCl_3$ at 400 MHz, TMS as an internal standard. Mass spectra were recorded on Shimadzu LC-MS using ionization technique. The elemental analysis was conceded out on Thermo Finnigan, CHNS analyzer. The growth of the reaction was monitored by TLC. All the chemicals were purchased from Avra, spectrochem, Alfa aeser chemicals. All melting points were recorded on shimadzu digital melting point apparatus.

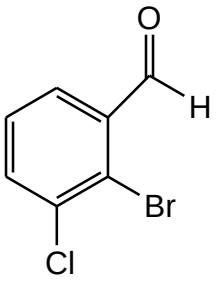
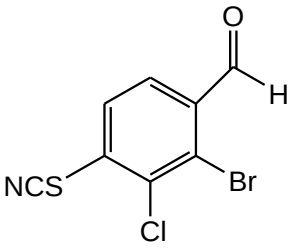
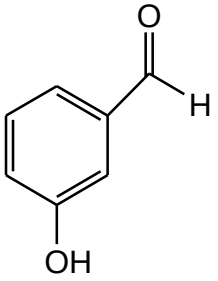
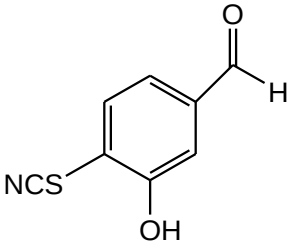
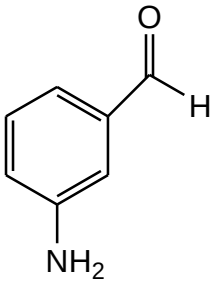
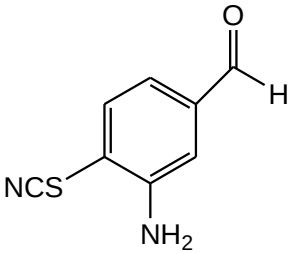
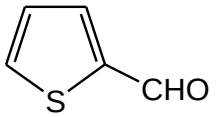
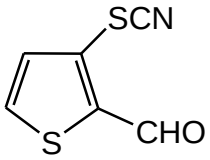
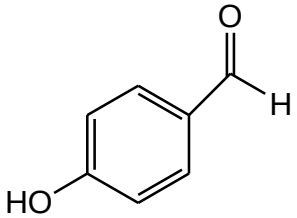
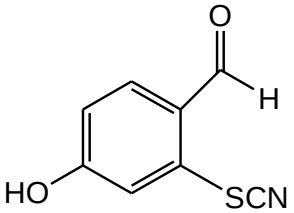
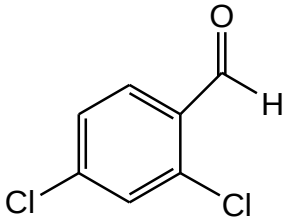
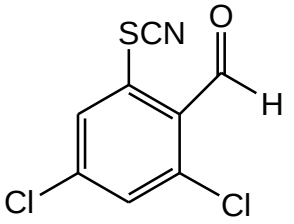
IV. GENERAL PROCEDURE

To a mixture of aryl aldehyde (5mmol) and ammonium thiocyanate (10mmol) and 1-ethyl-3-methyl imidazolium chloride/zinc chloride was added as catalyst. The mixture was stirred at room temperature for appropriate time in presence of acetonirtile as a solvent. Development of reaction was monitored by TLC. After completion of reaction solid product formed which is further recrysallised using ethanol to get pure product. Yield of this procedures are high in very short reaction time and RTIL catalyst was recovered by distillation and recycled upto three times for further use.

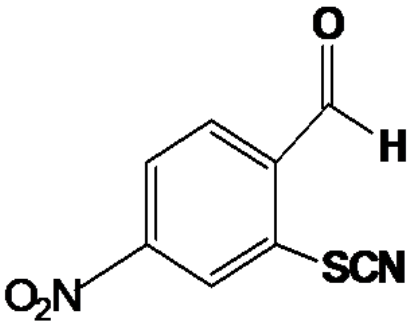
Thiocyanation of aromatic aldehydes using ionic liquid

Entry	Substrate	Product	Reaction Time (min.)	Yield (%)	M.P. (^{0}C)

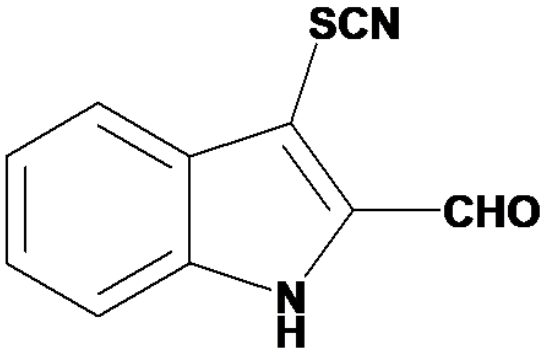
a			52	80	241-243
b			54	85	179-181
c			34	75	168-170
d			38	89	187-189
e			30	92	146-148
f			55	79	188-190
g			32	96	192-194

h			40	80	189-191
i			42	84	163-165
j			45	83	177-179
k			30	90	169-171
l			35	94	156-158
m			27	81	164-166

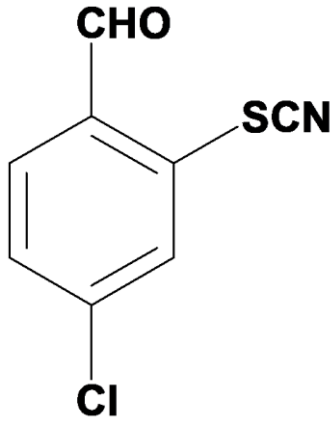
Spectral data of thiocyanated compounds



(f) IR-(cm^{-1}): 3107(Ar. C-H), 2065(SCN), 1716(C=O), 1541(-NO_2), 1346(C=C)
^{1}HNMR- ($CDCl_3$)δ: 10.1(s,1H), 8.40(d,1H), 8.12(s,1H), 8.10(d,1H)
^{13}CNMR -($CDCl_3$)δ: 190.4, 151.0,140.0,130.5, 111.1,124.3
Mass -(m/z): 209.3($m^{+\cdot}$), 219.1,224.2



(g) IR-(cm^{-1}): 3164(N-H),2817(Ar. C-H),2065(SCN),1635(C=O),1519(C=C),
^{13}HNMR -($CDCl_3$)δ: 7.63(d 1H);7.64(d 1H);7.79(d 1H);7.80(d 1H);9.61(d 1H);10.46(s 1H)
Mass -(m/z): 201.3($m^{+\cdot}$),218.2,274.5,301.4



(a) ^{1}HNMR- ($CDCl_3$)δ: 7.14(d 1H);7.37(s 1H);7.38(d 1H);10.42(s 1H)
^{13}CNMR -($CDCl_3$)δ: 113.28,127.98,130.08,131.80,132.38,133.87,146.48,191.38
Mass -(m/z): 211.7($m^{+\cdot}$),239.9,287.9,337.9,369.9

V. CONCLUSION

We have developed very easy and convenient procedure for thiocyanation of aromatic substituted aldehydes. The catalyst used ethyl methyl imidazolium chloride is non toxic for environment. The reagent used ammonium thiocyanate is very easily available. We observed that, further purification was not necessary of products, just by recrystallising with ethanol product becomes pure. Yield of this procedures are high in very short reaction time to complete this reaction. The advantages of this methodology environmentally benign, simple workup, recyclable and reusable catalyst.

VI. REFERENCES

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