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AN EFFICIENT GRINDSTONE TECHNIQUE FOR ELECTROPHILIC THIOCYANATION OF AROMATIC AND HETEROAROMATIC COMPOUNDS USING THIOCYANATE IN PRESENCE OF ICl /$KHSO_4$AND KIO_4/$KHSO_4$

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ABSTRACT

Grindstone technique has been found to be a highly efficient for thiocyanation of aromatic and heteroaromatic compounds with Iodine mono chloride/$KHSO_4$, Potassium metaperiodate/ $KHSO_4$. The methods offered selective thiocyanation of aromatic and heteroaromatic compounds in good yields with remarkable rate accelerations. The developed protocols under nonconventional (sonication and grindstone) methods are also promising compared with the existing procedures.

Keywords: Potassium metaperiodate; Potassium bisulfate; Iodine mono chloride, Ammonium thiocyanate; Selective thiocyanation; Grindstone technique; rate accelerations.

INTRODUCTION

Interest in the thiocyanate products is connected mainly with their wide range of antifungal, antitumor, antiparasitic activities[1-3]. Several thiocyanate compounds found their use as important synthons in organic, pharmaceutical, medicinal and agriculture chemistry[4-10]. These compounds can be easily converted to other functional groups such as thiocarbamate[4], aryl nitrile[5], sulfide[5], and thionitrile[7], which have been used as precursors for dyes, drugs, agrochemicals and also used in the preparation of several anticancer agents[8, 9]. Over a period of time, several efficient regioselective thiocyanation methods have been put forwarded. Certain noteworthy eco-friendly thiocyanation protocols include: ammonium thiocyanate/oxone[10], H_2O_2/H_5IO_6/KSCN in aqueous media[11], chemo selective thiocyanation of anilines and indoles using H_2O_2/Boron sulfonic acid with KSCN[12], thiocyanation of aromatics and heteroaromatics with molecular iodine[2], ammonium thiocyanate on montmorillonite K-10 clay[13] at 80°C, NH_4SCN/Ce(IV)ammonium nitrate[14] at room temperature, NH_4SCN/iodic acid[15],NH_4SCN/trichloroisocyanuric acid/wet SiO_2, green and recyclable catalyst [2-(Sulfoxy)ethyl]sulfamic acid[17], H_2O_2/NH_4SCN in presence of a reusable nanomagnetic Fe_3O_4 catalyst[18], N-thiocyanatosuccinimide[19], green and efficient KSCN/silica sulfuric acid and H_2O_2/silica boron sulfonic acid[20]. In addition to the above, $Zn(SCN)_2$/Cl_2, $Mn(OAc)_3$, $AlCl_3$/under solvent free conditions, Al_2O_3,$FeCl_3$, Para-Toluene Sulfonic Acid, poly (4-vinylpyridine)-supported thiocyanate/$K_2S_2O_8$, diphenyl phosphinite ionic liquid, diethyl azodicarboxylate, and Poly[4-diacetoxyiodo] Styrene are also used as reagents and/or catalysts for thiocyanation of aromatics[20-30]. On the other hand, nucleophilic thiocyanation of aromatic compounds using hypervalent iodine reagents[31], copper perchlorate[32], and electrochemical thiocyanation[32-37]of aromatic and heteroaromatic compounds have also been reported. Recently from our laboratory we have reported the thiocyanation of aromatic compounds and heteroaromatic compounds using Zeolite H-Sdusy powder (Cbv-720)[38], Ammonium metavanadate[39] under conventional and non-conventional conditions.

In continuation of our search for the design and execution of potential thiocyanation protocols, we have focused our attention on iodine compounds[40]. Iodine is a versatile element, which adopts a variety of

oxidation states, commonly ranging from (formally) I(VII) to I(-I), including the intermediate states of I(V), I(III) and I(I). Iodine is a good Lewis acid, and forms a charge-transfer complex with a wide range of electron donors. Potassium metaperiodate (KIO_4) is a heptavalent iodine versatile reagent, which is used in oxidation of vast variety of inorganic[40-43], organic substrates[44,45] and several other synthetic protocols[46-50]. On the other hand, Iodine monochloride (ICl) is also a monovalent iodine compound [I(I)]. Iodine behaves as a source of I^+ due to the difference in the electronegativity of iodine and chlorine[51]. It is being employed as a source of electrophilic iodine in the synthesis of certain aromatic iodides[52] and electrophilic cyclizations[53-56].

Green chemistry principles, put forwarded by Anastas and Warner[37] highlighted the importance of economically viable and environmentally safe methods in synthetic organic chemistry, and became the main driving force to several chemists to take up organic synthesis under solvent-free conditions. Grindstone chemistry is one such method, which is not only simple, but also satisfies both economic and environmental demands by replacing toxic solvents[58-60]. Recent reviews and publications proved that "Grindstone" technique is a highly greener and rapid method for the preparation of organic compounds without the complicacies associated with the use of different solvents, including water. Organic reactions performed under solvent-free conditions have gained remarkable importance due to their enhanced selectivity, mild reaction conditions and associated ease of manipulation.

The use of solid acid catalysis is potentially more attractive because of the ease of removal and recycling of the catalyst and the possibility that the solid might influence the selectivity. In search of our continued interest for the development of eco-friendly synthetic protocols in electrophilic substitution reactions, we have developed present methodology for thiocyanation of aromatic and heteroaromatic compounds under conventional and ultrasonication conditions, using potassium metaperiodate (KIO_4), and iodine monochloride (ICl) in presence of $KHSO_4$. We have done the reactions under mineral acid free conditions using $KHSO_4$. Potassium bisulfate ($KHSO_4$) is a commonly used desktop laboratory reagent that creates *insitu* acidic environment due to the complete protolysis of the ion HSO_4^- and functions as the source of H^+ ions, without decomposition. Periodate anion is the highest in the oxyanion series of iodine with iodine existing in hypervalent oxidation state (VII). Unlike other perhalogenates, such as perchlorate, it can exist in two forms: ortho Periodate (IO_6^{5-}) and metaperiodate (IO_4^-).

EXPERIMENTAL

All the chemicals were purchased from Aldrich or Arcos Organics and used without further purification. Analytical TLC was carried out using Merck aluminum-backed 0.2 mm silica gel 60 F-254 plates. Column chromatography was conducted using Merck silica gel 60 (230-400mesh). Perkin Elmer FT-IR and Varian VNMRS-400 MHz spectrometers were used for recording Infrared (IR) and ^{1}HNMR spectra. Chemical shifts are reported as values in ppm relative to $CHCl_3$ (7.26), and TMS was used as internal standard. BUCHI B-545 capillary melting point apparatus is used for the determination of melting points.

General procedure for synthesis of thiocyanates

For thiocyanation, the contents such as ammonium thiocyanate (0.2 mol) mixed with aromatic or heteroaromatic compound (0.1 mol), $KHSO_4$ (0.1 mol), catalytic amounts of KIO_4 or ICl (0.4–0.5 mol percentage),and solvent (acetonitrile, 25mL) were taken in a dried round bottom flask and stirred for about 15 to 20 hours at room temperature. After complete conversion as indicated by TLC, the reaction mixture was quenched with water, and is treated with dilute $NaHCO_3$ solution, followed by the addition of ethyl acetate. The organic layer was separated, dried over Na_2SO_4 and concentrated under vacuum, purified with column chromatography using hexane: ethyl acetate as eluent to get pure product. Products are characterized by spectroscopic data. Representative NMR spectroscopic data are presented in Table-6.

Ultrasonically assisted synthesis of thiocyanates

Catalytic amounts of KIO_4 or (0.4–0.5 mol percentage) was added to a mixture of ammonium thiocyanate (0.2 mol), aromatic or heteroaromatic compound (0.1 mol), $KHSO_4$ (0.1 mol) in acetonitrile solvent, and were taken in a conical flask. The resulting mixture irradiated with ultra sound for the appropriate time

given in Table-3. The progress of the reaction was monitored by TLC. Work-up procedure to obtain the products is almost similar to the one discussed in earlier section.

Grindstone synthesis of thiocyanates

Catalytic amounts of KIO_4 or ICl (0.4–0.5 mol percentage), ammonium thiocyanate (0.2 mol), aromatic or heteroaromatic compound (0.1 mol), $KHSO_4$ (0.1 mol) are taken in a mortar and ground with pestle under solvent free conditions. The progress of the reaction was monitored by TLC. Remaining work-up procedure to obtain the products is largely similar to the one discussed in earlier section. Obtained results from all the methods are presented Tables-4 and 5.

RESULTS AND DISCUSSION

Thiocyanation of 1H-indole was investigated as a model reaction to study the effect of solvent on reaction rates. For chosen a better solvent, we have examined thiocyanation of indole in various solvents such as DCE, DCM, MeOH, $CHCl_3$, THF and acetonitrile. The yields obtained for these reactions demonstrated that acetonitrile was found to be favorable solvent for thiocyanation reaction, and the data compiled in Table-1. In order to establish the catalyst (KIO_4, ICl) optimal conditions, we have chosen aniline as a model for thiocyanation reaction.

Table-1: Effect of solvent on thiocyanation reaction of Indole using KIO_4

Entry	Solvent	Yield (%)
1	DCE	65
2	DCM	62
3	MeOH	68
4	$CHCl_3$	55
5	THF	44
6	MeCN	80

Reactions did not proceed either in the absence either $KHSO_4$ or iodine-catalyst (KIO_4 or ICl). However, the reactions took place smoothly in the presence of both the additives $KHSO_4$ or iodine-catalyst. Maximum product is obtained when 0.4equivalents of KIO_4 or ICl was employed as iodine- catalyst, as shown Tables-2 and 3. This observation clearly indicates that both acidic environment and oxidizing catalyst are required along with ammonium thiocyanate for electrophilic thiocyanation. We have investigated thiocyanation reaction with different aromatic and heterocyclic compounds containing electron-rich and electron-deficient groups. The reactions afforded corresponding thiocyanate derivatives in good to excellent yields (Scheme-1).

Table-2: Catalyst optimization for thiocyanation of aniline

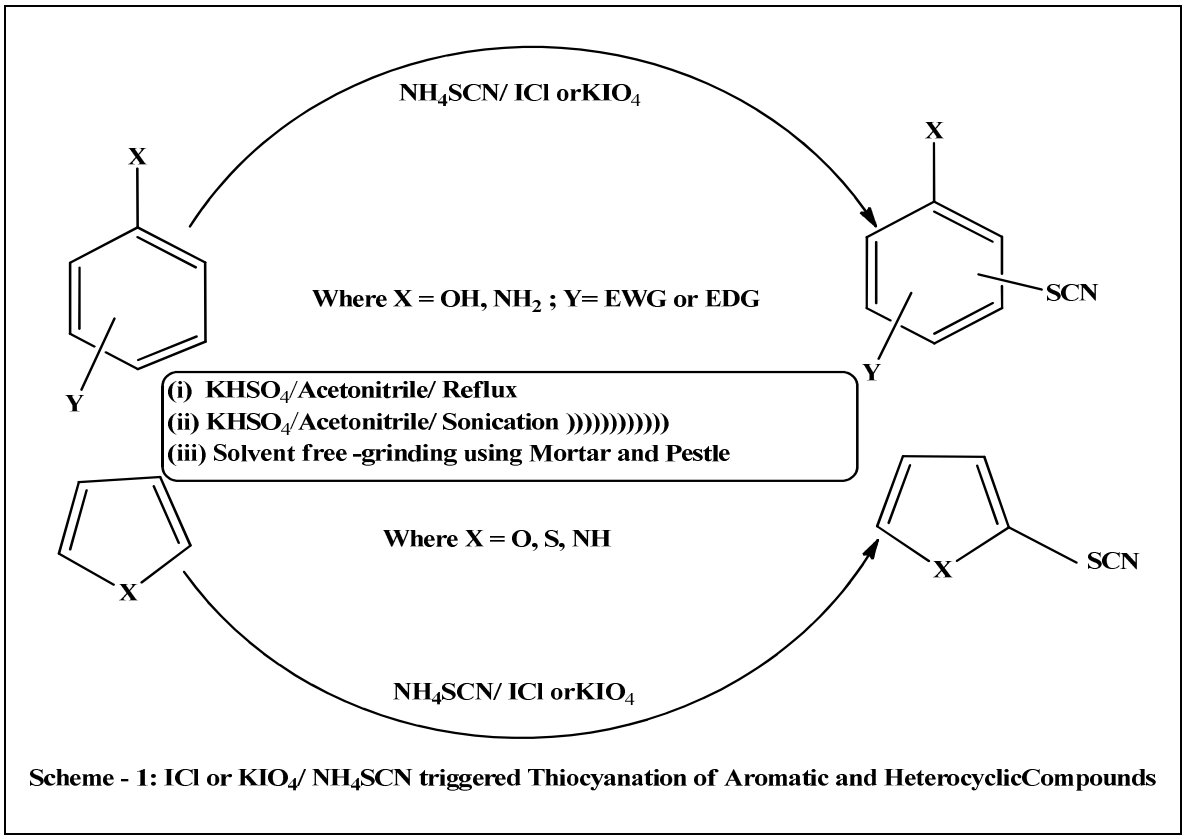
Entry	Amount of catalyst (gms)	Yield (%)	
		KIO_4	ICl
1	0.05	25	15
2	0.1	28	24
3	0.15	32	35
4	0.2	40	48
5	0.25	50	64
6	0.4	72	75
7	0.5	72	75

Data presented in Tables-4 and 5 showed that, indole and 2-Methyl indole gave corresponding thiocyanated products in excellent yields. While in the conversion of 5-Bromo indole to5-Bromo 3-

thiocyanato indole using ammonium thiocyanate in presence of $KHSO_4/KIO_4$, and $KHSO_4$/ICl, the reactions required longer reaction time.

Table-3: Comparison of the isolated yields for the thiocyanation of Aniline to 4-thiocyanato aniline with reported classical methods.

Catalyst	Reaction conditions	R.T. (min)	Yield (%)	Reference
KIO_4/ NH_4SCN/ $KHSO_4$	(Solvent-free) Grinding	8.0	85	Present Work
KIO_4/ NH_4SCN/ $KHSO_4$	USAR in MeCN	25	80	Present Work
ICl/ NH_4SCN/ $KHSO_4$	(Solvent-free) Grinding	9	76	Present Work
ICl/ NH_4SCN/ $KHSO_4$	USAR in MeCN	23	82	Present Work
Zeolite-H-SDUSY/ NH_4SCN	USAR in MeCN	90	78	38
NH_4VO_3/NH_4SCN/ $KHSO_4$	USAR in MeCN	(35-40)	79	39(a)
Copper powder/NH_4SCN	------	-----	56	39(b)
Aryldiazonium salt/NH_4SCN	------	-------	80	39(c)



Scheme - 1: ICl or KIO_4/ NH_4SCN triggered Thiocyanation of Aromatic and HeterocyclicCompounds

Table-4: Thiocyanation of aromatic and heteroaromatic compounds using $KIO_4$and $KHSO_4$ (Isolated yields)

Entry	Substrate	Product	Conventional		Sonication		Grinding	
			R. T (hrs)	Yield (%)	R. T (min)	Yield (%)	R.T. (min)	Yield (%)
1	Aniline	4:2-Thiocyanatoaniline	16	72:12	25	75:15	8	80:15
2	*o*-Cl aniline	2-Chloro 4-Thiocyanatoaniline	15	75	20	72	8	86
3	*m*-OMe aniline	3-Methoxy 4-Thiocyanatoaniline	15	78	25	73	9	84
4	N-Methyl aniline	4-Thiocyanato N-methylaniline	17	70	30	74	10	78
5	N, N dimethyl aniline	4-Thiocyanato N, N-dimethylaniline	18	68	40	81	10	75

6	Phenol	2:4-Thiocyanato phenol	19	70:10	45	79:15	10	80:12
7	*p*-Br phenol	4-Bromo 2-thiocyanatophenol	19	75	40	80	9	84
8	*p*-Cl Phenol	4-Chloro 2-thiocyanatophenol	18	75	35	77	10	88
9	Pyrrole	2-Thiocyanato 1H-pyrrole	16	80	30	72	9	92
10	Furan	2-Thiocyanato furan	16	78	35	90	8	90
11	Thiophene	2-Thiocyanato thiophene	15	80	20	79	8	90
12	Indole	3-Thiocyanato 1H-indole	15	80	25	77	9	92
13	5-Br indole	5-Bromo 3-thiocyanato indole	19	65	45	68	10	78
14	2-Me indole	2-Methyl 3-thiocyanato indole	16	78	40	80	9	86
15	N-Methyl indole	3-thiocyanato N-Methyl- indole	16	70	30	71	8	78
16	Diphenyl amine	4-Thiocyanato diphenylamine	20	64	45	61	9	72

Table-5: Thiocyanation of aromatic and heteroaromatic compounds using ICl and $KHSO_4$ (Isolated yields)

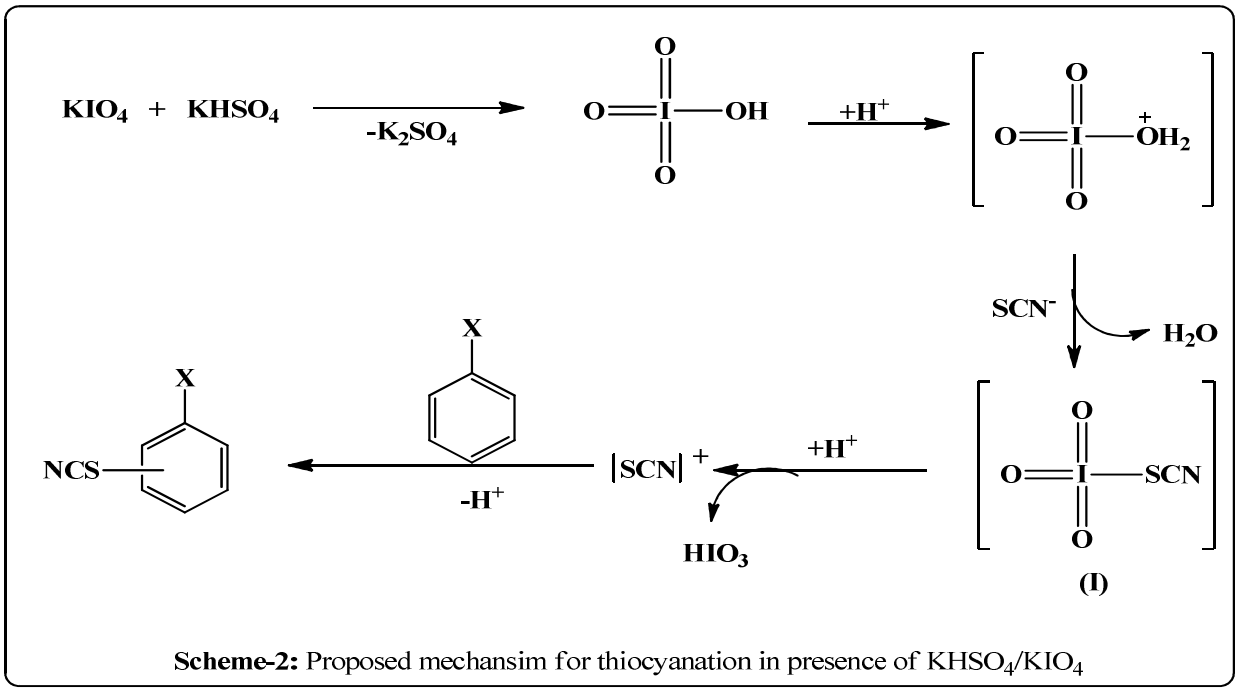
Entry	Substrate	Product	Conventional		Sonication		Grinding	
			R. T (hrs)	Yield (%)	R. T (min)	Yield (%)	R.T. (min)	Yield (%)
1	Aniline	4:2-Thiocyanatoaniline	15	74:14	23	82:10	9	76:15
2	*o*-Cl aniline	2-Chloro 4-Thiocyanatoaniline	15	77	18	89	8	73
3	*m*-OMe aniline	3-Methoxy 4-Thiocyanatoaniline	14	76	24	86	10	81
4	N-Methyl aniline	4-Thiocyanato N-methylaniline	18	71	28	79	9	79
5	N, N dimethyl aniline	4-Thiocyanato N, N-dimethylaniline	17	72	39	76	8	83
6	Phenol	2:4-Thiocyanato phenol	18	79:10	45	80:15	8	84:12
7	*p*-Br phenol	4-Bromo 2-thiocyanatophenol	16	88	40	84	9	79
8	*p*-Cl Phenol	4-Chloro 2-thiocyanatophenol	17	77	36	91	7	77
9	Pyrrole	2-Thiocyanato 1H-pyrrole	18	86	31	94	8	80
10	Furan	2-Thiocyanato furan	15	85	29	91	8	91
11	Thiophene	2-Thiocyanato thiophene	14	81	19	93	10	81
12	Indole	3-Thiocyanato 1H-indole	15	88	25	95	9	78
13	5-Br indole	5-Bromo 3-thiocyanato indole	16	88	42	80	8	71
14	2-Me indole	2-Methyl 3-thiocyanato indole	14	91	37	89	7	76
15	N-Methyl indole	3-thiocyanato N-Methyl- indole	15	79	27	85	7	77
16	Diphenyl amine	4-Thiocyanato diphenylamine	18	69	41	79	7	64

This is due to the fact that the lower electron density of such substrates and lower yield is attributed probably due to steric hindrance. It is interesting to note that ortho substituted aromatic compounds underwent thiocyanation only at the para position, while para substituted compounds gave ortho thiocyanated products. Heteroaromatic compounds such as Pyrrole, Furan and Thiophene were also easily converted into the corresponding monothiocyanated products with excellent yields. Aromatic amines were readily furnished the monothiocyanated derivatives with high para-selectivity.

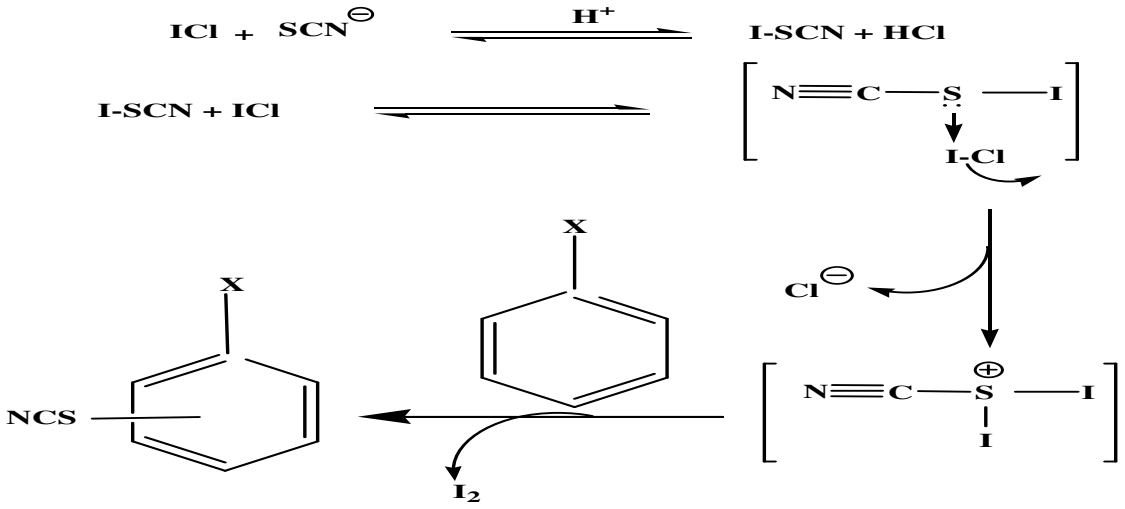
N-substituted amines such as N-methyl aniline, N,N-dimethylaniline were transformed into the corresponding aryl thiocyanates in good yields. A plausible mechanism for the electrophilic thiocyanation of the aromatic compound is depicted in Scheme-2.

In situ generation of periodic acid is due to the interaction of oxidant KIO_4 and $KHSO_4$, thus produced periodic acid *in situ* interacts with H^+ causes removal of water, which then reacts with thiocyanate ion produce species (I). In presence of H^+, SCN^+ is obtained. This cationic species reacts with aromatic compound, afforded the corresponding thiocyanate derivative.

When iodine monochloride (ICl) is used as catalyst, mechanism for thiocyanation of the aromatic compound could be explained as shown in Scheme-3.



Scheme-2: Proposed mechansim for thiocyanation in presence of $KHSO_4/KIO_4$



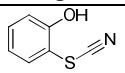
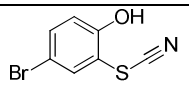
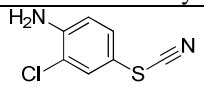
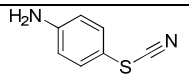
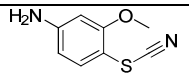
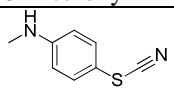
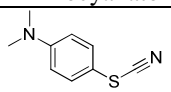
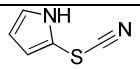
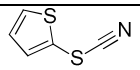
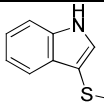
Scheme-3: Proposed mechanism for thiocyanation in presence of ICl/$KHSO_4$

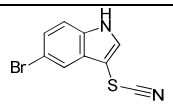
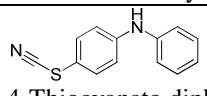
Iodine monochloride converted to iodine thiocyanate (ISCN) followed by the elimination of HCl by picking up the *in situ* generated H^+ ion due to the dissociation of $KHSO_4$. Iodine thiocyanate (ISCN) thus produced could then generate a cationic $(I_2SCN)^+$ intermediate. In a fast step the active $(I_2SCN)^+$ reacts with aromatic compound to afford corresponding thiocyanate derivative.

Another interesting feature in our studies is the effect of sonication on the rate of thiocyanation observed in ultrasonically assisted reactions. Rate accelerations of the ultrasonically assisted thiocyanation reactions in the present study are due to cavitation phenomena[40-43], a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid. Cavitation is a process in which mechanical activation destroys the attractive forces of molecules in the liquid phase. When the sample is subjected to sonication, ultrasound waves propagate into the liquid media resulting in

alternating high-pressure (compression) and low-pressure (rare faction) cycles. During rarefaction, high-intensity sonic waves create small vacuum bubbles in the liquid, which then collapse violently during compression, creating very high local temperatures in the liquid and enhance mass transfer. The reaction times were reduced under conventional stirred conditions from 15-20 hrs to about 20–45 min in ultrasonically assisted condition. It is of interest to note that the results obtained in the present study are comparable with some of the earlier reports, which can be seen from the data presented in Table 3, indicating that the present methodology is also a sincere effort in the development of new eco-friendly protocol for thiocyanation of aromatic compounds.

Table-6: NMR spectroscopic data for representative compounds

S.No.	Compound	NMR data
1.	 2-Thiocyanato phenol	^{1}H NMR ($CDCl_3$): δ 7.14 (d, J = 8.1 Hz, 1H), 6.73 (m, J = 7.9 Hz,2H), 6.54 (d, J = 8.1 Hz, 1H), 4.83 (s, 1H).m/z= 151.
2.	 4-bromo-2-thiocyanato-phenol	^{1}H NMR ($CDCl_3$): δ 7.22 (s, 1H), 7.03 (d, J = 8.1 Hz, 1H),6.53 (d, J = 8.1 Hz, 1H), 4.84 (s, 1H).m/z= 230.
3.	 2-Choloro-4-thiocyanatoaniline	^{1}H NMR ($CDCl_3$): δ 7.52 (d, J = 8.2 Hz, 2H), 7.26 (dd, J = 8.1 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 4.37 (brd s, 2H). m/z= 184 (m.p. 59–61◦C).
4.	 4-Thiocyanatoaniline	^{1}H NMR ($CDCl_3$): δ 7.38 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 3.94 (brd s, 2H), 13C NMR (75 Hz, $CDCl_3$): δ 148.7, 134.3, 116.1, 112.3, 109.5, m/z = 150 (m.p.51–54◦C.)
5.	 3-Methoxy 4-Thiocyanatoaniline	^{1}H NMR ($CDCl_3$): δ 7.29 (d, J = 8.3 Hz, 1H), 6.28 (dd, J = 8.3 Hz, 1H), 6.24 (d, J = 8.2 Hz, 1H), 3.98 (s, 2H), 3.87 (s, 3H).m/z = 180 (m.p. 99–101◦C)
6.	 4-Thiocyanato N-methylaniline	^{1}H NMR ($CDCl_3$): δ 7.37 (d, J = 8.64 Hz, 2H), 6.59 (d, J = 8.68 Hz, 2H), 4.11 (brd s, 1H), 2.85 (s, 3H). m/z= 164.
7.	 4-Thiocyanato N, N-dimethylaniline	^{1}H NMR ($CDCl_3$): δ 7.44 (d, J = 8.8 Hz, 2H), 6.66(d, J = 8.8 Hz, 2H), 3.02 (s, 6H), ^{13}C NMR (75 MHz, $CDCl_3$): 151.5, 134.3, 113.2, 112.9, 106.4, 40.2. m/z= 178 (m.p. 72–74◦C).
8.	 2-Thiocyanato 1H-pyrrole	^{1}H NMR ($CDCl_3$): δ 6.27 (dd, H, J = 3Hz, J = 6.3 Hz), 6.64 (m, 1H, J = 1.5 Hz, J = 3.6 Hz, J = 3.9 Hz), 6.96 (m, 1H, J = 1.5 Hz, J = 3Hz, J = 4.5 Hz), 8.9 (s, 1H), ^{13}CNMR(75 MHz, $CDCl_3$): δ 124.3, 120.1, 111.1, 110.9, 102.8. m/z= 124.
9.	 2-Thiocyanato thiophene	^{1}H NMR ($CDCl_3$): δ 7.45–8.10 (m, 3H).
10.	 3-Thiocyanato 1H-indole	^{1}H NMR ($CDCl_3$): δ 7.30 (m, 2H, J = 9.9 Hz, J = 6.9 Hz), 7.42 (m, 1H, J = 9.9 Hz, J = 7.2 Hz), 7.48 (d, 1H, J = 3 Hz), 7.09 (dd, 1H, J = 5.7 Hz, J = 3Hz), 8.72 (br s, 1H), ^{13} C NMR (75 MHz, $CDCl_3$): δ 135.9, 131.1, 127.4, 123.7, 121.8, 118.5, 112.3, 112.1, 91.53. m/z= 174. (mp 72–73◦C).

11.	 5-Bromo 3-thiocyanato indole	^{1}H NMR ($CDCl_3$): δ 8.87 (br s, 1H), 7.92–7.15 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 134.6, 132.2, 129.3, 123.1, 121.2, 115.4, 113.7, 111.9, 102.2 (m/z) =251(M-1), 253 (M+2) (mp 126–127◦C).
12.	 4-Thiocyanato diphenylamine	^{1}H NMR ($CDCl_3$): δ 7.43 (d, J = 8.1 Hz, 2H), 7.34 (t, J =8.2 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.08 (t, J = 8.2 Hz, 1H), 7.03 (d, J = 8.2 Hz, 2H), 5.94(brd s, 1H). m/z= 226 (m.p. 62–63◦C).

CONCLUSION

In summary, we have developed two simple, novel and ecofriendly synthetic protocols for the thiocyanation of aromatic and heteroaromatic compounds using ammonium thiocyanate in presence of $KHSO_4$ and ICl or KIO_4. The reactions afforded corresponding thiocyanates with good yields under reflux conditions. Rates of these reactions were enhanced from several hours (15-20 hrs) to 20-45 min under ultrasonication, and 8 to 10 minutes with grind–stone technique. Developed methods are simple and mild protocols, which provide easy work up procedure and high product yields.

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