Review Article

Journal of Chemistry Letters
journal homepage: www.jchemlett.com
ISSN (online): 2717-1892

Metal-Free Regioselective Thiocyanation of (Hetero) Aromatic C-H Bonds using Ammonium Thiocyanate: An Overview

Soma Majedi [a, *], Lakashima Sreerama,[b] Esmail Vessally [c], Farnaz Behmagham [d]

[a] *College of Health Sciences, University of Human Development, Sulaimaniyah, Kurdistan region of Iraq*
[b] *Department of Chemistry, Qatar University, Qatar*
[c] *Department of Chemistry, Payame Noor University, Tehran, Iran*
[d] *Miyandoab Branch , Islamic Azad University, Miyandoab, Iran*

ARTICLE INFO

Article history:
Received 5 April 2020
Received in revised form 10 May 2020
Accepted 4 June 2020
Available online 4 June 2020

Keywords:
Organosulfur compounds
Aryl thiocyanates
Ammonium thiocyanate
Direct functionalization of C-H bonds
Metal-free reactions

ABSTRACT

(Hetero)aryl thiocyanates have been extensively used as dyes, insecticides, vulcanization accelerators, and building blocks in the synthesis of diverse organosulfur compounds. Therefore, development of novel, efficient, and practical methods for their synthesis has always been the important topic in organic synthesis. Recently, direct thiocyanation of (hetero)aromatic C-H bonds using inexpensive and easily available ammonium thiocyanate has attracted considerable attention from the organic synthesis community, because no pre-functionalization of the starting materials is required and therefore the hazardous waste streams are significantly reduced. In this review, we summarize the recent discoveries and developments in this interesting field by hoping it will inspire and stimulate further research on the topic.

1. Introduction

Organosulfur compounds are among the most important class of molecules due to their presence in extensive number of natural products and biologically active compounds [1, 2].

Interestingly, more than 285 FDA-approved drugs contain at least one sulfur atom in their structure [3]. In this family of compounds, aryl thiocyanates are extremely valuable building blocks in organic chemistry and they allow to access efficiently various sulfur-containing compounds such as thiophenols, disulfides, aryl sulfides, trifluoromethylated sulfides, aryl sulfoxides, phosphonothioates, sulfenyl-tetrazoles and many more (Figure 1). Therefore, efficient strategies for the synthesis of this important class of organosulfur compounds have drawn extraordinary attention all the time.

Direct C-H bond activation with subsequent C-S bond formation has recently emerged as a powerful method for the synthesis of organosulfur compounds because of its high step- and atom-economical property [5].

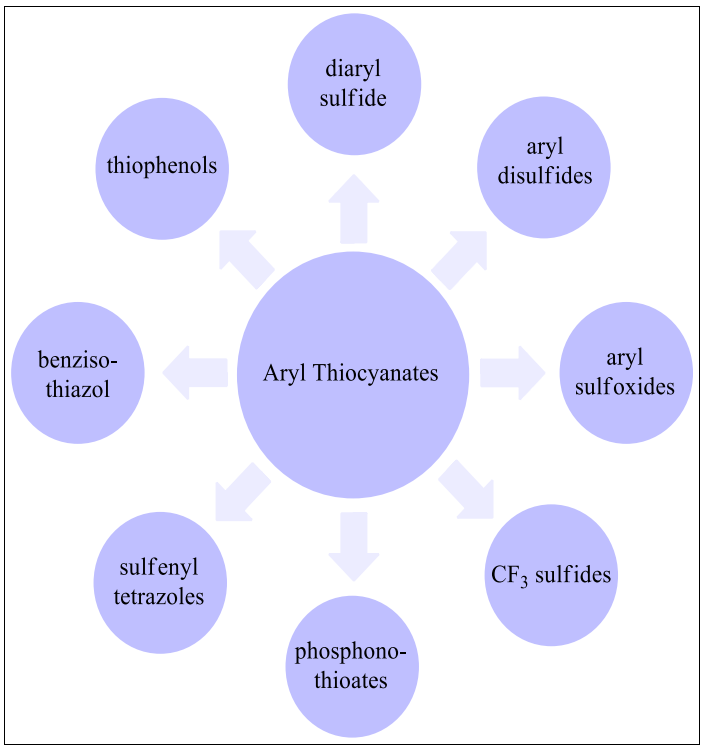


Figure 1. Some of synthetic products from aryl thiocyanates

* Corresponding author, e-mail: soma.majedi@uhd.edu.iq

Along this line, numerous protocols have been developed which allow highly efficient synthesis of aryl thiocyanates through the direct thiocyanation of aromatic C-H bonds with various thiocyanating reagents such as NaSCN [6], KSCN [7], NH_4SCN [8], $(SCN)_2$ [9], TMSCN [10], *N*-thiocyanatosaccharin [11], and *N*-thiocyanatosuccinimide [12]. Among them, ammonium thiocyanate (NH_4SCN) is the cheapest and most frequently used one. Synthesis of aryl thiocyanate derivatives *via* electrophilic thiocyanation of the corresponding aromatic compounds with NH_4SCN offers several advantages, including: (i) shorter synthetic routes; (ii) high atom economy; (iii) nontoxic by-products; (iv) eco-friendly process; and (v) ease of handling. Interesting is the fact that most of the reported examples on this interesting synthetic strategy has been performed under metal-free conditions which made this route of aryl thiocyanates synthesis more sustainable and greener. In connection with our recent works on the modern organic synthesis [13], we summarize here variety of protocols for the synthesis of (hetero)aryl thiocyanates through metal-free direct thiocyanation of (hetero)aromatic C-H bonds with commercially available, inexpensive NH_4SCN (Figure 2), by hoping it will inspire and stimulate further research on the topic.

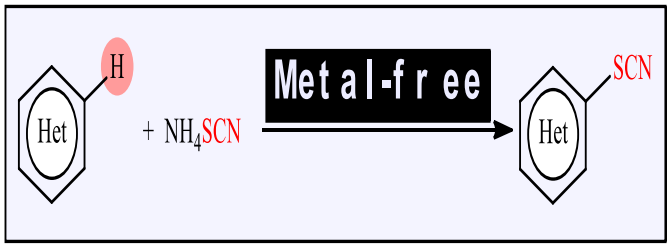
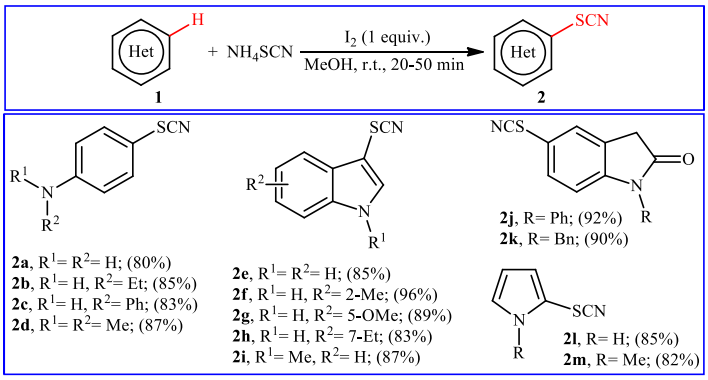


Figure 2. Metal-free regioselective thiocyanation of (hetero)aromatic C-H bonds with NH_4SCN

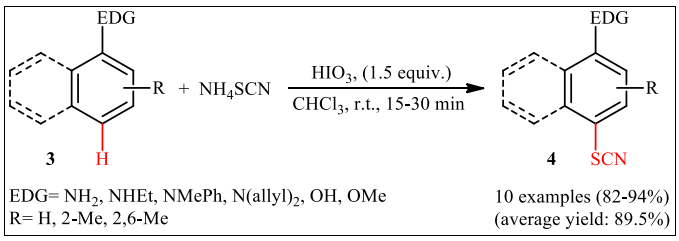
2. Iodine-mediated reactions

In 2004, Yadav and co-workers reported one of the earliest protocols for the metal-free direct thiocyanation of (hetero)aromatic C-H bonds with ammonium thiocyanate [14]. To assessing the efficiency of different oxidants, 2-methylindole was chosen as the model substrates. Among the various oxidants such as DDQ, I_2, $Mn(OAc)_3{\bullet}2H_2O$, $Bi(NO_3)3{\bullet}5H_2O$ and $C_6H_5I(OAc)_2$; molecular iodine was found to be more effective, which gave a better yield of 3-thiocyanato-indole product. Thus, in the presence of stoichiometric amounts of I_2 in MeOH at room temperature, thiocyanation of various electron-rich (hetero)aromatic compounds **1** with NH_4SCN furnished the corresponding (hetero)aryl thiocyanates **2** in good to excellent yields with excellent mono-selectivity (Scheme 1). Some important information of the reactions are listed below: (i) in the cases of pyrroles, indoles, and oxindoles, substitution took place selectively at the 2-, 3-, 5-positions, respectively; (ii) The reaction proceeded with very excellent regioselectivity for *para*-position of aryl amines and provided corresponding 4-thiocyanatoanilines; (iii) both N-protected and NH-free indoles were compatible in this transformation; and (iv) although minor amounts of 2,4-dithiocyanated products were obtained by using pyrrole substrates, no bis-thiocyanation was observed in the cases of indoles, oxindoles and aromatic amino compounds. Four years later, the same authors improved the efficiency of their methodology in the terms of reaction time and product yields by performing the process in the presence of *o*-iodoxybenzoic acid (IBX) in MeCN [15].



Scheme 1. I_2-mediated direct thiocyanation of (hetero)arenes **1** with NH_4SCN

Inspired by these works, Ulhas and Akamanchi reported that in the presence of 1.5 equiv. of iodic acid (HIO_3) in $CHCl_3$ at room temperature, thiocyanation of various arenes **3** bearing electron-donating groups with NH_4SCN furnished the corresponding 4-thiocyanato-arenes **4** in high to excellent yields (Scheme 2) [16]. Heteroaromatic compounds including indole and thiophene were also easily transformed into the mono-thiocyanated products using this procedure. However, electron-deficient aromatic substrates, such as nitrobenzene and benzoic acid, failed to enter into this C-S bond forming reaction.

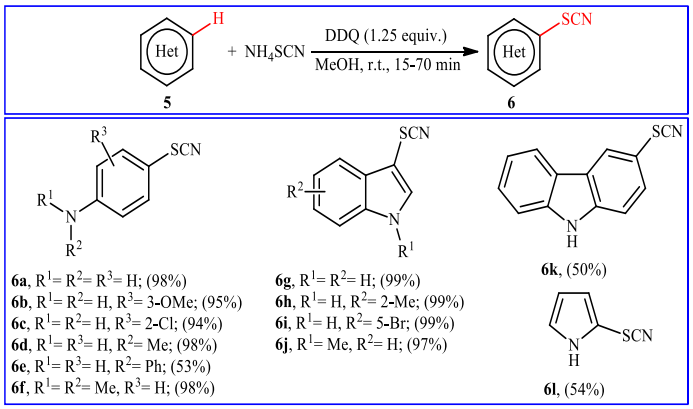


Scheme 2. Ulhas-Akamanchi's synthesis of 4-thiocyanato-arenes **4**

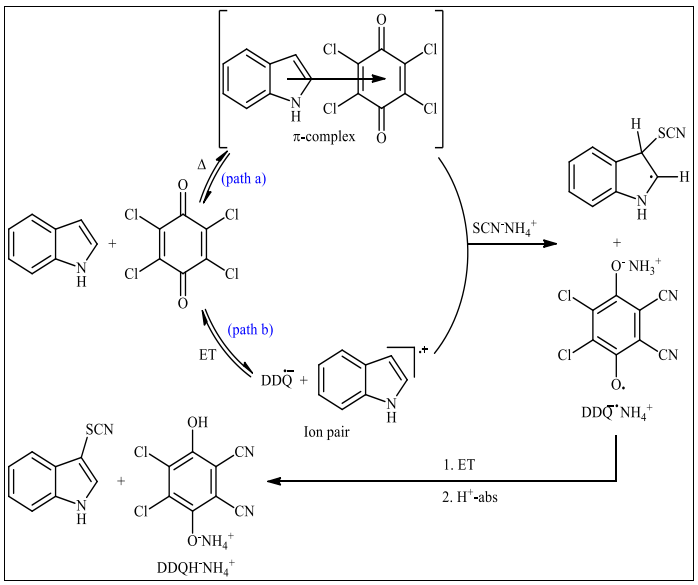
3. DDQ-mediated reactions

In 2007, Memarian and Baltork along with their colleagues reported that 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) can act as effective oxidant for the direct synthesis of aryl thiocyanates from the corresponding arenes under mild reaction conditions [17]. For a comparison purpose, they tested the thiocyanation of 2-methylindole with NH_4SCN in the

presence of 1.5 equiv. of DDQ in various solvents (e.g., *n*-hexane, H_2O, MeOH, H_2O-MeOH, DMF, MeCN, DCM, $CHCl_3$, EtOAc) at room temperature and found that methanol was the best choice for this conversion. Under the optimized conditions, a variety of (hetero)arenes **5** react to give the corresponding (hetero)aryl thiocyanates **6** in moderate to almost quantitative yields (Scheme 3). According to the authors proposed mechanism (Scheme 4), the reaction starts by either the formation of a π-complex *via* charge-transfer transition between aromatic system and DDQ (path a) or an ion-pair intermediate, namely the radical cation of aromatic system and $DDQ^{\bullet-}$, through an electron-transfer process between aromatic system and DDQ. Next, nucleophilic attack of thiocyanate ion (SCN^-) to one of these intermediates lead to the formation of radical of thiocyanated system accompanied by $DDQ^{\bullet-}$. Finally, an electron transfer from the radical intermediate to $DDQ^{\bullet-}$ followed by the proton abstraction, affords the target thiocyanated product and $DDQH{\bullet}NH_4^+$. The next year, this research team improved the efficiency of this thiocyanation reaction by performing the process under sonic waves [18].



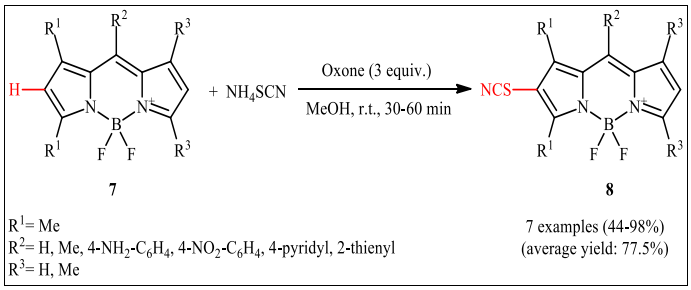
Scheme 3. DDQ-mediated thiocyanation of (hetero)arenes **5** with NH_4SCN



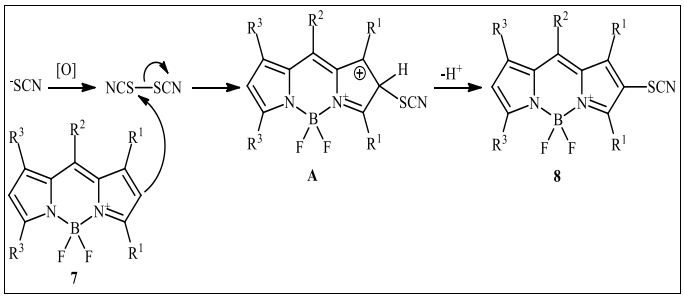
Scheme 4. Mechanistic proposal for the formation of (hetero)aryl thiocyanates **6**

4. Oxone-mediated reactions

In 2015, Emery and co-workers studied the possibility of synthesizing thiocyanated boron-dipyrromethene (BODIPY) dyes **8** through the direct thiocyanation of the respective 1,3-dimethyl BODIPYs **7** with NH_4SCN (Scheme 5) [19]. In their optimization study, the authors found that the use of 3 equiv. of oxone in MeOH at room temperature gave the best results. The reaction was highly selective at the C2-position of the BODIPYs and tolerated sensitive functional groups such as nitro and amino functionalities. It should be mentioned that the same reaction condition was also used for the direct thiocyanation of 3-amino BODIPYs. In this case, the insertion occurred selectively at C5-position. The author proposed mechanism for this reaction is depicted in Scheme 6. Unfortunately, the addition of a thiocyanato group did not greatly influence the spectroscopical features of the BODIPYs studied. The authors nicely solved this problem by conversion of thiocyanated BODIPYs to the corresponding thioalkylated derivatives.

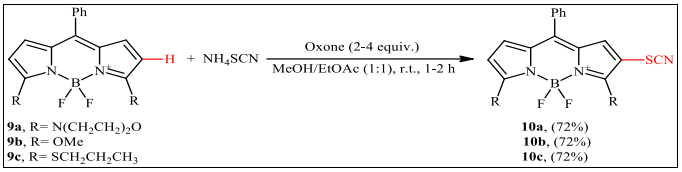


Scheme 5. Emery's synthesis of thiocyanated boron-dipyrromethene dyes **8**



Scheme 6. Mechanistic proposal for the reaction in Scheme 5

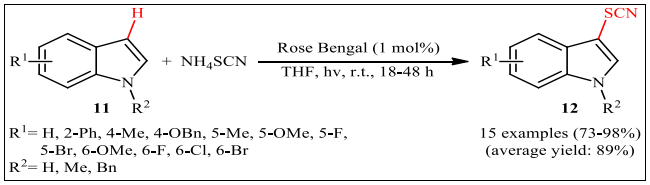
Recently, in a closely related investigation, Rezende's research group also reported the synthesis of a small library of C2-thiocyanated BODIPYs **10** through the direct thiocyanation of 3,5-disubstituted BODIPY dyes **9** with NH_4SCN using oxone (2-4 equiv.) as an oxidant in binary solvent MeOH/EtOAc with ratio 1:1 (Scheme 7) [20]. The thiocyanation of 3-substituted BODIPYs were also successfully performed, and the C5-thiocyanato derivatives were obtained in good yields. Interestingly, when larger excesses of the thiocyanating reagent and oxidant were used, double thiocyanated products were obtained.



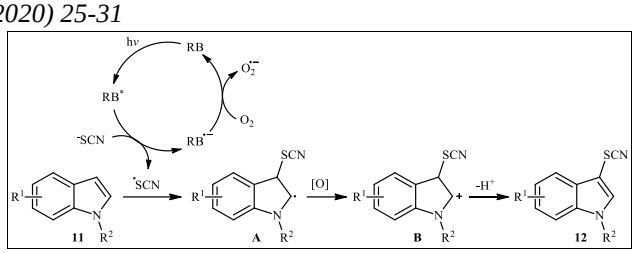
Scheme 7. Direct thiocyanation of 3,5-disubstituted BODIPY dyes **9** with NH_4SCN using oxone as an oxidant

5. Visible light-induced reactions

In 2014, Li and co-workers reported the first example of visible-light-induced direct thiocyanation of aromatic C-H bonds with NH_4SCN under metal-free conditions [21]. They showed that the treatment of indole derivatives **11** with 3 equiv. of NH_4SCN in the presence of only 1 mol% of commercially available inexpensive organic dye, Rose Bengal (RB) in THF under visible light irradiation at room temperature gave the corresponding 3-thiocyanato-1*H*-indoles **12** in good to excellent yields, ranging from 73% to 98% (Scheme 8). Noteworthy, other photocatalysts, such as $Ru(bpy)_3Cl_2{\cdot}6H_2O$, $Ru(bpy)_3(PF_6)_2$, $Ir(ppy)_3$, and Eosin Y were also found to promote this C-S bond forming reaction; albeit, in lower yields. The results revealed that both electron-donating group substituted indoles and indoles bearing weak electron-withdrawing groups (e.g., F, Cl, Br) worked well under the optimized conditions. However, indoles bearing strong electron-withdrawing groups (e.g., NO_2) were not compatible under the reaction conditions and no desired products were obtained. The protocol is also applicable for *N*-substituted indoles, such as *N*-methyl-, *N*-phenyl-, and *N*-benzyl indoles. However, the reaction of *tert*-butyl indole-1-carboxylate did not occur due to the electron-withdrawing effect of Boc group. The mechanism proposed to explain this C-S bond formation starts with the formation of excited state of RB* *via* the excitation of RB under visible light irradiation, which reacts with ^-SCN to produce $^{\cdot}SCN$ radical and generates $RB^{\cdot-}$ radical anion. The photoredox cycle is completed by the molecular oxygen oxidation of $RB^{\cdot-}$ to the ground state RB. Next, an electrophilic addition of $^{\cdot}SCN$ to indole **11** occurs, leading to intermediate **A** which after oxidation gives cation intermediate **B**. Finally, rearomatization of intermediate **B** by losing a proton affords the expected 3-thiocyanoindole product **12** (Scheme 9). Very recently, Gao, Liu, and Wan applied this procedure for the first vinyl C-H bond thiocyanation reaction of tertiary enaminones with NH_4SCN [22].

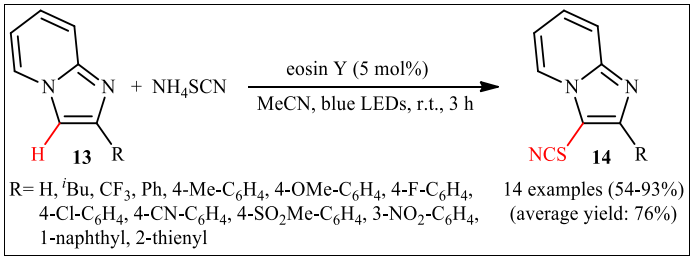


Scheme 8. Visible-light-induced Rose Bengal catalyzed C-3 thiocyanation of indoles **11** with NH_4SCN



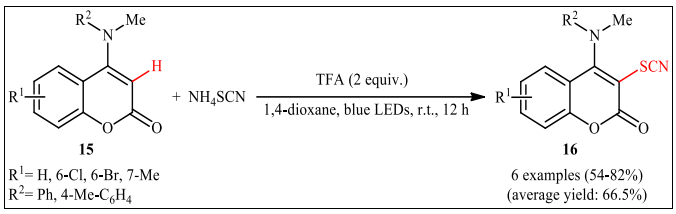
Scheme 9. Plausible mechanism for the formation of 3-thiocyanato-1*H*-indoles **12**

In 2015, Hajra's research group disclosed a green and elegant protocol for visible-light- mediated regioselective C-3 thiocyanation of imidazo[1,2-*a*]pyridines **13** with NH_4SCN under metal-free conditions at room temperature (Scheme 10) [23]. The authors investigated the reaction variables such as photocatalyst, solvent, and oxidant and found that performing the reaction in the presence of a catalytic amount of eosin Y in MeCN under ambient air and irradiation of blue LED light (425 nm) was the optimum reaction condition. The reaction is particularly noteworthy as the authors demonstrated impressive functional group tolerance, including F, Cl, Br, OH, CN, NO_2, CF_3, sulfone, and ether functionalities. The procedure is also applicable for the synthesis of 3-thiocyanato-imidazo[1,2-*a*]pyridines **14** on gram-scale. Other imidazoheterocycles like imidazo[2,1-*b*]thiazole and benzo[*d*]imidazo[2,1-*b*]thiazole were also compatible in this transformation and gave the desired products in high yields.



Scheme 10. Hajra's synthesis of 3-thiocyanato-imidazo[1,2-*a*]pyridines **14**

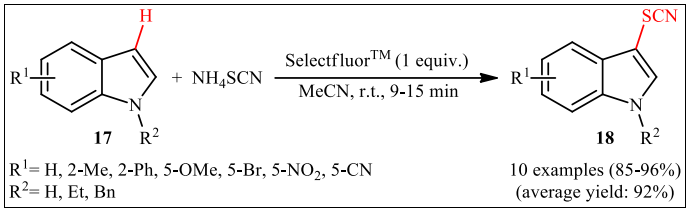
In an innovative investigation, Yang and co-workers showed that a library of C3-thiocyanated 4-(phenylamino)-2*H*-chromen-2-one derivatives **16** were successfully formed from the reaction of 4-(phenylamino)-2*H*-chromen-2-ones **15** with NH_4SCN under visible light irradiation in the absence of any photocatalyst (Scheme 11) [24]. By screening of various additives (e.g., HOAc, TFA, H_2O, HCl) and solvents (e.g., 1,4-dioxane, toluene, DMSO, DMF, MeCN, DCE, H_2O, EtOH) they found that performing the reaction in the presence of 2 equiv. of TFA in 1,4-dioxane at room temperature was the optimum reaction condition. It should be mentioned that the presence of aromatic amine at the C4-position of substrates were crucial for the success of this C-H functionalization reaction. No desired product was obtained when phenylamino group was replaced by H, NH_2, and OH groups.



Scheme 11. Photocatalyst-free regioselective C−H thiocyanation of 4-anilinocoumarins **15** with NH_4SCN under visible light conditions

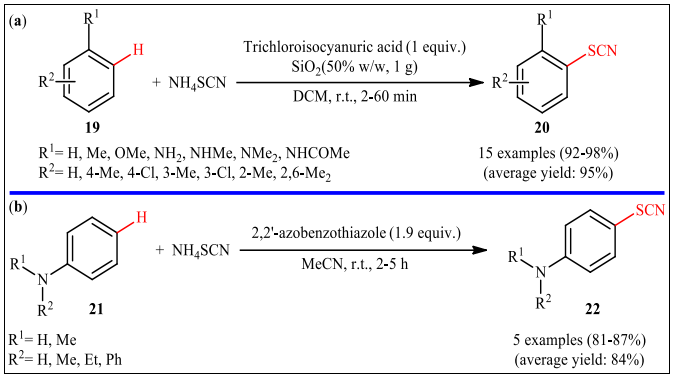
6. Miscellaneous reactions

After pioneering work by Chakrabarty and Sarkar on montmorillonite K10 clay mediated direct thiocyanation of a small series of indoles with NH_4SCN under metal-free conditions [25], Yadav and co-workers disclosed a general and practical protocol for the direct and site-selective thiocyanation of various N-protected and NH-free indoles with 1 equiv. of NH_4SCN using a stoichiometric amount of Selectfluor™ as a mediator [26]. In this study, ten 3-thiocyanato-1*H*-indole derivatives **18** were efficiently synthesized in excellent yields through the C3-selective functionalization of the corresponding indoles **17** under ambient temperature within 9-15 min (Scheme 12). Interestingly, electronic character of the substituents on the indole ring had a remarkably little effect on the rate of this reaction. Generally, both electron-donating and electron-withdrawing groups were well tolerated under this condition. Two years later, Das and Kumar found that *para*-toluene sulfonic acid could also successfully promote this reaction under metal-free conditions [27]. Along this line, Wang and He applied a similar strategy for the thiocyanation of a library of indoles by using a catalytic amount of thiourea in combination with N-chlorosuccinimide (NCS) [28].

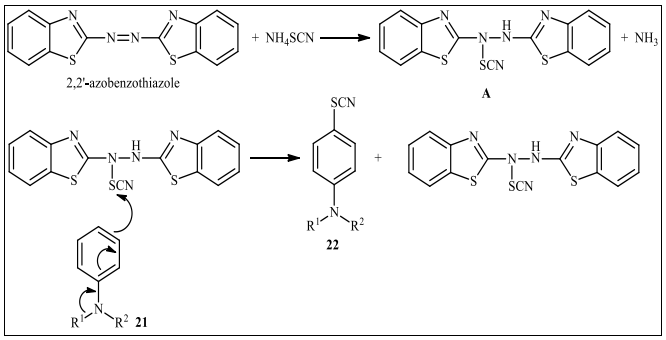


Scheme 12. Site-selective thiocyanation of indoles **17** with NH_4SCN in the presence of Selectfluor™

In 2012, the group of Akhlaghinia reported an interesting mono- and regioselective thiocyanation of simple electron-rich arenes **19** (toluene, xylenes, anisoles, anilines, acetanilide, and *p*-chloroacetanilide) with NH_4SCN employing trichloroisocyanuric acid/wet SiO_2 combination as a catalytic oxidation system and DCM as a solvent [29]. This thiocyanation proceed under very mild reaction conditions and selectively provided *para*-thiocyanated products **20** in excelent yields (Scheme 13a). The protocol was also applicable to naphthalene and heteroaromatic scaffolds. Unfortunately, the authors did not comment on the possible mechanistic pathway of the reaction. Concurrently, Iranpoor and co-workers discovered that treatment of unsubstituted aromatic amines **21** with 3 equiv. of NH_4SCN in the presence of 2,2'-azobenzothiazole as a heterogeneous oxidant in dry MeCN afforded the corresponding 4-thiocyanatoanilines **22** in high yields (Scheme 13b) [30]. However, the reaction did not work with substituted aromatic amines (e.g., 3-aminophenol). Of note, other electron-rich arenes such as phenol and anisole failed to inter into this C-S bond formation reaction. The author proposed mechanism for the formation of 4-thiocyanated anilines is shown in Scheme 14. Shortly afterwards, Nikoofar and Gorji demonstrated that nano SiO_2 also could facilitate the metal-free thiocyanation of various heteroaromatic compounds and anilines with NH_4SCN [31].



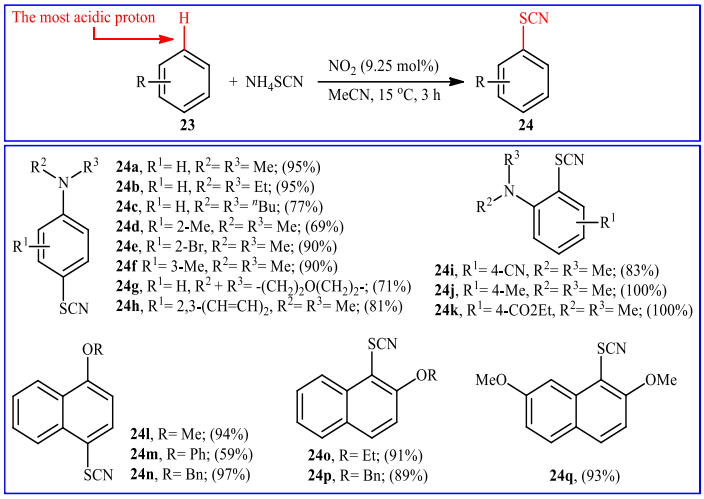
Scheme 13. (a) Metal-free regioselective thiocyanation of simple arenes **19** with NH_4SCN reported by Akhlaghinia (b) *para*-selective thiocyanation of anilines **21** with NH_4SCN in the presence of 2,2'-azobenzothiazole



Scheme 14. Proposed mechanism for the reaction in Scheme 14b

Following these works, Ren and Wang along with their co-workers developed a highly efficient NO_2-catalyzed regioselective thiocyanation reaction of electron-rich arenes **23** with NH_4SCN using O_2 as the terminal oxidant under mild conditions (Scheme 15) [32]. The reactions were run in MeCN at 15 °C, tolerated various electron-donating and electron–with-drawing functional groups, and generally provided mono-thiocyanated products **24** in moderate to high yields. Besides arenes, thiophenes could also be used as substrates in this synthetic procedure. However, N- and O-heteroaromatics such as imidazole, benzofuran, and

dibenzo[*b*,*d*]furan were not compatible with this reaction. According to the authors proposed mechanism, one of the most probable mechanism pathways involves the aromatic radical cation and the catalytic species NO^+.



Scheme 15. NO_2-catalyzed regioselective thiocyanation reaction of electron-rich arenes **23** with NH_4SCN developed by Ren and Wang

In this concern, Bhat *et al.* [33] successfully used $K_2S_2O_8$ as a commercially available and inexpensive oxidant for direct and regioselective thiocyanation of phenols, anilines and heterocycles (e.g., thiophenes, indoles) with NH_4SCN in DCM at room temperature. They also applied their procedure for high yielding synthesis of GW501516, a most potent and selective peroxisome proliferator-activator receptor δ (PPARδ) agonist.

7. Conclusion

The direct introduction of the thiocyanate (SCN) group into the aromatic molecule represents the more attractive approach for the synthesis of aryl thiocyanates. In this sense, in 1941, Wood and Fieser reported for the first time the direct thiocyanation of arene C-H bonds using the highly toxic thiocyanogen (NCS-SCN) under metal-free conditions. Since then, various groups of scientists around the world have devoted their attention to the development of environmentally friendly, stable, and efficient thiocyanating reagents. Today, numerous thiocyanating reagents are commercially available. Ammonium thiocyanate is the cheapest one that is extensively utilized for this transformation. As illustrated, various aromatic and heteroaromatic C-H bonds could be regioselectively thiocyanated using this reagent under mild and metal-free conditions. Importantly, most of the reactions covered in this review could be scaled up and performed on multigram scales without difficulty. It is our hope that this review will encourage organic chemists to develop novel and extremely efficient methods for the synthesis of (hetero)aryl thiocyanates.

References

[1] S. Petropoulos, F. Di Gioia, G. Ntatsi, Vegetable organosulfur compounds and their health promoting effects, Curr. Pharm. Des., 23 (2017) 2850-2875.

[2] M. Feng, B. Tang, S. H Liang, X. Jiang, Sulfur containing scaffolds in drugs: synthesis and application in medicinal chemistry, Curr. Top. Med. Chem., 16 (2016) 1200-1216.

[3] K.A. Scott, J.T. Njardarson, Analysis of US FDA-approved drugs containing sulfur atoms, Top. Curr. Chem., 376 (2018) 5.

[4] T. Castanheiro, J. Suffert, M. Donnard, M. Gulea, Recent advances in the chemistry of organic thiocyanates, Chem. Soci. Rev., 45 (2016) 494-505.

[5] C. Shen, P. Zhang, Q. Sun, S. Bai, T.A. Hor, X. Liu, Recent advances in C–S bond formation via C–H bond functionalization and decarboxylation, Chem. Soci. Rev., 44 (2015) 291-314.

[6] (a) S. Jana, S. Chattopadhyay, Efficient and novel method for nucleophilic thiocyanation of activated aromatic compounds using sodium thiocyanate at ambient condition, Inorg. Chem. Commun., 35 (2013) 160-163; (b) F. Wang, X. Yu, Z. Qi, X. Li, Rhodium-catalyzed C-S and C-N functionalization of arenes: Combination of C-H activation and hypervalent iodine chemistry, Chem. Eur. J., 22 (2016) 511-516.

[7] (a) N. Muniraj, J. Dhineshkumar, K.R. Prabhu, N-Iodosuccinimide catalyzed oxidative selenocyanation and thiocyanation of electron rich arenes, ChemistrySelect, 1 (2016) 1033-1038; (b) D. Khalili, Graphene oxide: a promising carbocatalyst for the regioselective thiocyanation of aromatic amines, phenols, anisols and enolizable ketones by hydrogen peroxide/KSCN in water, New J. Chem., 40 (2016) 2547-2553.

[8] (a) K. Nikoofar, S. Gorji, Oxidant-free thiocyanation of phenols and carbonyl compounds under solvent-free conditions by $AlCl_3/NH_4SCN$, J. Sulfur Chem., 37 (2016) 80-88; (b) V.A. Kokorekin, R.R. Yaubasarova, S.V. Neverov, V.A. Petrosyan, Electrooxidative C–H functionalization of heteroarenes. thiocyanation of pyrazolo [1, 5-*a*] pyrimidines, Eur. J. Org. Chem., (2019) 4233-4238.

[9] (a) T. Nagamachi, P. Torrence, J. Waters, B. Witkop, An easy access to 5-mercaptopyrimidine nucleosides through one-step synthesis of 5-thiocyanato-uridine and-2′-deoxyuridine, Chem. Commun., (1972) 1025-1026; (b) S.-I. Watanabe, T. Ueda, Thiocyanation of tubercidin and its derivatization to 6-propyl-and 6-cyano derivatives, Nucleos. Nucleot. Nucl., 1 (1982) 191-203.

[10] (a) Y. Kita, T. Takada, S. Mihara, B.A. Whelan, H. Tohma, Novel and direct nucleophilic sulfenylation and thiocyanation of phenol ethers using a hypervalent iodine (III) reagent, J. Org. Chem., 60 (1995) 7144-7148; (b) C. Feng, Y. Peng, G. Ding, X. Li, C. Cui, Y. Yan, Catalyst and additive-free regioselective oxidative C–H thio/selenocyanation of arenes and heteroarenes with elemental sulfur/selenium and TMSCN, Chem. Commun., 54 (2018) 13367-13370.

[11] D. Wu, J. Qiu, P.G. Karmaker, H. Yin, F.-X. Chen, N-Thiocyanatosaccharin: a “sweet” electrophilic thiocyanation reagent and the synthetic applications, J. Org. Chem., 83 (2018) 1576-1583.

[12] (a) K. Jouvin, C. Matheis, L.J. Goossen, Synthesis of aryl tri-and difluoromethyl thioethers *via* a C-H-thiocyanation/fluoroalkylation cascade, Chem. Eur. J., 21 (2015) 14324-14327; (b) S.N. Kadam, A.N. Ambhore, M.J. Hebade, R.D. Kamble, S.V. Hese, M.V. Gaikwad, P.D. Gavhane, B.S. Dawane, Metal-Free One-Pot Chemoselective thiocyanation of imidazothiazoles and 2-aminothiazoles with *in situ* generated N-thiocyanatosuccinimide, Synlett, 29 (2018) 1902-1908.

[13] J. Wang, P. Su, S. Abdolmohammadi, E. Vessally, A walk around the application of nanocatalysts for cross-dehydrogenative coupling of C–H bonds, RSC Adv., 9 (2019) 41684-41702; (b) S. Ebrahimiasl, F. Behmagham, S. Abdolmohammadi, R.N. Kojabad, E. Vessally, Recent advances in the application of nanometal catalysts for Glaser coupling, Curr. Org. Chem., 23 (2019) 2489-2503; (c) M. Li, S. Abdolmohammadi, M.S. Hoseininezhad-Namin, F. Behmagham, E. Vessally, Carboxylative cyclization of propargylic alcohols with carbon dioxide: A facile and green route to α-methylene cyclic carbonates, J. CO_2 Util., 38 (2020) 220-231; (d) Y. Yang, D. Zhang, E. Vessally, Direct amination of aromatic CH bonds with free amines, Top. Curr. Chem., 378 (2020) 37.

[14] J. Yadav, B. Reddy, S. Shubashree, K. Sadashiv, Iodine/MeOH: a novel and efficient reagent system for thiocyanation of aromatics and heteroaromatics, Tetrahedron Lett., 45 (2004) 2951-2954.

[15] J.S. Yadav, B.V.S. Reddy, B.B.M. Krishna, IBX: a novel and versatile oxidant for electrophilic thiocyanation of indoles, pyrrole and arylamines, Synthesis, 2008 (2008) 3779-3782.

[16] U.S. Mahajan, K.G. Akamanchi, Facile method for thiocyanation of activated arenes using iodic acid in combination with ammonium thiocyanate, Synth. Commun. 39 (2009) 2674-2682.

[17] H.R. Memarian, I. Mohammadpoor-Baltork, K. Nikoofar, DDQ-promoted thiocyanation of aromatic and heteroaromatic compounds, Can. J. Chem., 85 (2007) 930-937.

[18] H.R. Memarian, I. Mohammadpoor-Baltork, K. Nikoofar, Ultrasound-assisted thiocyanation of aromatic and heteroaromatic compounds using ammonium thiocyanate and DDQ, Ultrason. Sonochem., 15 (2008) 456-462.

[19] L.C.D. de Rezende, S.M.G. de Melo, S. Boodts, B. Verbelen, W. Dehaen, F. da Silva Emery, Thiocyanation of BODIPY dyes and their conversion to thioalkylated derivatives, Org. Biomol. Chem., 13 (2015) 6031-6038.

[20] L.C. Rezende, S.M. Melo, S. Boodts, B. Verbelen, F.S. Emery, W. Dehaen, Thiocyanation of 3-substituted and 3,5-disubstituted BODIPYs and its application for the synthesis of new fluorescent sensors, Dyes Pigm., 154 (2018) 155-163.

[21] W. Fan, Q. Yang, F. Xu, P. Li, A visible-light-promoted aerobic metal-free C-3 thiocyanation of indoles, J. Org. Chem., 79 (2014) 10588-10592.

[22] Y. Gao, Y. Liu, J.-P. Wan, Visible light-induced thiocyanation of enaminone C–H bond to access polyfunctionalized alkenes and thiocyano chromones, J. Org. Chem., 84 (2019) 2243-2251.

[23] S. Mitra, M. Ghosh, S. Mishra, A. Hajra, Metal-free thiocyanation of imidazoheterocycles through visible light photoredox catalysis, J. Org. Chem., 80 (2015) 8275-8281.

[24] G. Li, Q. Yan, X. Gong, X. Dou, D. Yang, Photocatalyst-free regioselective C–H thiocyanation of 4-anilinocoumarins under visible light, ACS Sustain. Chem. Eng., 7 (2019) 14009-14015.

[25] M. Chakrabarty, S. Sarkar, A clay-mediated eco-friendly thiocyanation of indoles and carbazoles, Tetrahedron Lett., 44 (2003) 8131-8133.

[26] J. Yadav, B.S. Reddy, Y.J. Reddy, 1-Chloromethyl-4-fluoro-1, 4-diazoniabicyclo [2, 2, 2] octane bis (tetrafluoroborate) as novel and versatile reagent for the rapid thiocyanation of indoles, azaindole, and carbazole, Chem. Lett., 37 (2008) 652-653.

[27] B. Das, A.S. Kumar, Efficient thiocyanation of indoles using para-toluene sulfonic acid, Synth. Commun., 40 (2010) 337-341.

[28] C. Wang, Z. Wang, L. Wang, Q. Chen, M. He, Catalytic thiourea promoted electrophilic thiocyanation of indoles and aromatic amines with NCS/NH_4SCN, Chin. J. Chem., 34 (2016) 1081-1085.

[29] B. Akhlaghinia, A.-R. Pourali, M. Rahmani, Efficient and novel method for thiocyanation of aromatic compounds using trichloroisocyanuric acid/ammonium thiocyanate/wet SiO_2, Synth. Commun., 42 (2012) 1184-1191.

[30] N. Iranpoor, H. Firouzabadi, R. Shahin, D. Khalili, 2, 2′-Azobenzothiazole as a new recyclable oxidant for heterogeneous thiocyanation of aromatic compounds with ammonium thiocyanate, Synth. Commun., 42 (2012) 2040-2047.

[31] K. Nikoofar, S. Gorji, Determination of the promoting effect of nano SiO_2 and H_3PO_4@ nano SiO_2 in the thiocyanation of N-containing aromatic compounds under solvent-free conditions, J. Sulfur Chem., 36 (2015) 178-186.

[32] Y.L. Ren, W. Wang, B. Zhao, X. Tian, S. Zhao, J. Wang, F. Li, Nitrogen dioxide catalyzed oxidative thiocyanation of arenes with ambient air as the terminal oxidant, ChemCatChem, 8 (2016) 3361-3366.

[33] T.B. Mete, T.M. Khopade, R.G. Bhat, Transition-metal-free regioselective thiocyanation of phenols, anilines and heterocycles, Tetrahedron Lett., 58 (2017) 415-418.

How to Cite This Article

Majedi, Soma, et al. "Metal-Free Regioselective Thiocyanation of (Hetero) Aromatic CH Bonds using Ammonium Thiocyanate: An Overview." Journal of Chemistry Letters 1.1 (2020): 25-31.