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Recent Trends in Direct S-Cyanation of Thiols

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ABSTRACT

Organic thiocyanates have attracted considerable attention owing to their diverse biological activities and applications as powerful and versatile building blocks in a variety of synthetic transformations. Hence, the development of efficient and practical strategies for their preparation that benefit from simple, inexpensive, and easily accessible starting materials is of prime importance in organic synthesis. In this regards, the direct cyanation of S-H bonds in thiol derivatives has emerged as a powerful and straightforward method for the formation of thiocyanate functionality which avoids tedious multi-step synthesis and pre-functionalization of starting materials that often required in conventional approaches. The present review is an attempt to highlight the most important contributions toward the synthesis of organic thiocyanate *via* direct S-cyanation of corresponding thiols from 1976 to 2022.

1. Introduction

Organosulfur compounds, organic molecules that contain sulfur (sulphur), are prevalent in a broad spectrum of biological [1], pharmaceutical [2] and natural molecules [3]. Organic thiocyanates are one the specific class of organosulfur compounds which not only are prevalent in a wide variety of important classes of natural products (Scheme 1) [4] and synthetic bioactive molecules [5] but also used as extremely promising building blocks in organic synthesis due to their diverse reaction patterns. Specially, they can be converted into other useful sulfur functional groups (Scheme 2), such as thiols [6], disulfides [7], thioethers [8], thioesters [9], trifluoromethyl thioethers [10], S-thiocarbamates [11], and sulfonyl cyanides [12]. In light of the above-mentioned chemistry, the development of efficient and practical strategies for synthesis of organic thiocyanates that benefit from simple, inexpensive, and easily accessible starting materials is of prime importance in organic synthesis. Traditionally, thiocyanate functionality has been generally introduced by nucleophilic or electrophilic thiocyanation of organic molecules [13]. However, their accessibility has been limited by the availability and reactivity of the required precursors [14]. Recently, organic thiocyanate derivatives were synthesized by directly introducing cyano group into S-H bond of thiol substrates as a convenient method for carbon–sulfur bond formation. Beside high step economy, easy availability of starting material, simplicity, and broad substrate scope were other advantages of this synthetic strategy. In connection with our recent review papers on modern organic synthesis [15], we summarize here a variety of methods for the synthesis of organic thiocyanate from the corresponding thiols (Figure 1), with

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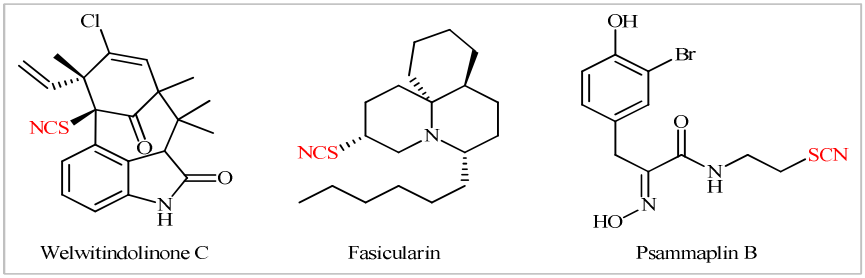
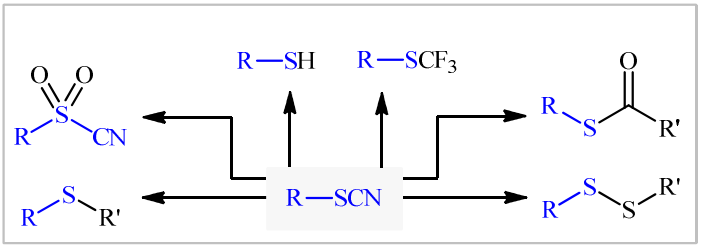


Scheme 1. Selected examples of SCN-containing natural molecules.



Scheme 2. elected examples on synthetic applications of organic thiocyanates.

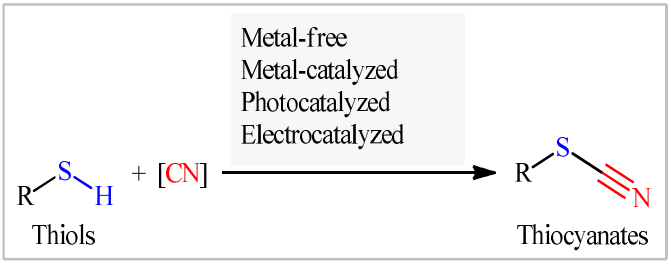
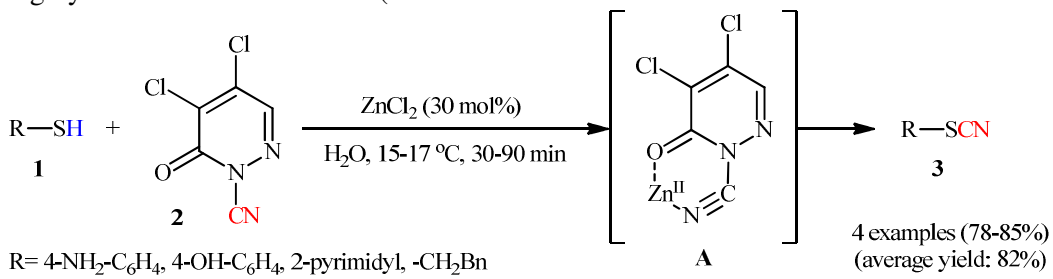


Fig. 1. Direct S-cyanation of thiols.

special emphasis on the mechanistic features of the reactions.

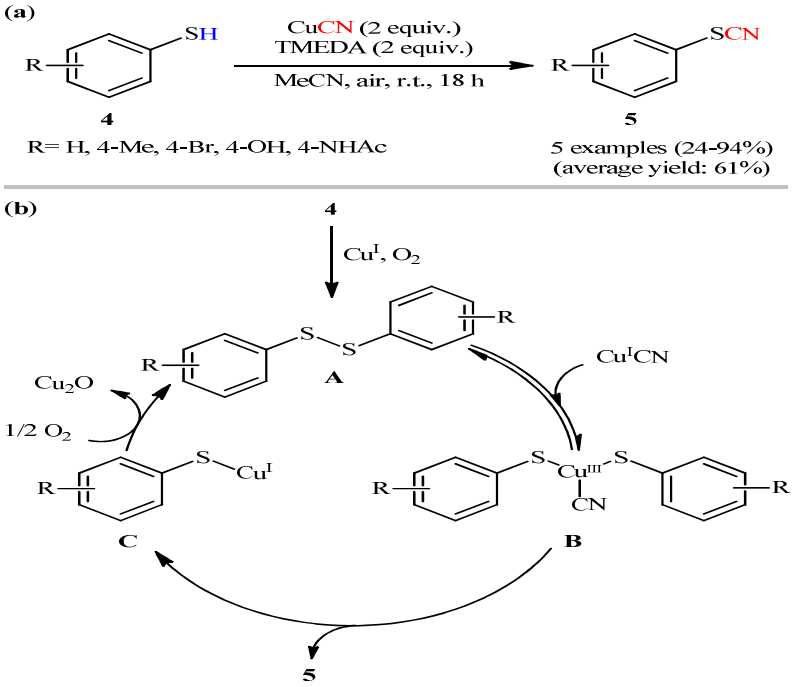
2. Metal-catalyzed reactions

One of the earliest reports on the synthesis of thiocyanates through the metal-catalyzed direct S-H cyanation of thiols was published by Cho, Yoon and co-workers in 2005 [16]. In this study, treatment of a small series of thiols **1** with 4,5-dichloro-6-oxopyridazine-1(6*H*)-carbonitrile **2** in the presence of a catalytic amount of $ZnCl_2$ in water, allowed the synthesis of respective thiocyanates **3** in high yields within the minutes (Scheme 3). According to the authors, $ZnCl_2$ may enhance the reactivity of cyano group by chelation with **2** at N-2 position. It should be mentioned that 5-chloro-4-methoxy-6-oxopyridazine-1(6*H*)-carbonitrile was also successfully applied as cyanating agent for the same set of thiols. Besides thiols, other nucleophiles (e.g., amines, β-diketones) were also chemoselectively cyanated in high yields under the optimal conditions. Interestingly, when 4-aminothiophenol was subjected to the reaction, the corresponding S-cyanated product was produced exclusively.



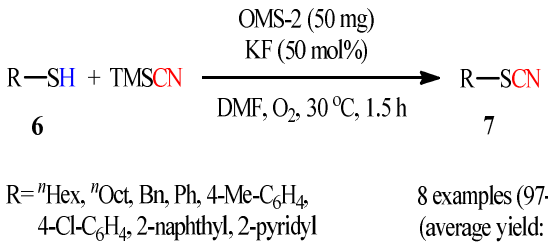
Scheme 3. $ZnCl_2$-catalyzed cyanation of thiols 1 with 4,5-dichloro-6-oxopyridazine-1(6*H*)-carbonitrile 2.

A decade later, Castanheiro *et al*. developed a convenient copper-mediated aerobic oxidative cyanation method to synthesize thiocyanates from thiol derivatives [17]. The reaction of thiophenols **4** with excess of CuCN, using *N*,*N*,*N*',*N*'-tetramethyl-1,2-ethylenediamine (TMEDA) as the ligand under the open air at room temperature could give the *S*-cyanateted products **5** in 24–94% yields (Scheme 4a). Under similar conditions, the cyanation with 4-nitrothiophenol proceeded sluggishly, even at near reflux temperature (80 °C). In accord to the presumed mechanistic pathway, this Cu-mediated oxidative cyanation proceeds through the following key steps (Scheme 4b): (i) initial formation of disulfide **A** *via* the oxidation of thiol **4** with the aim of copper; (ii) oxidative addition of CuCN into the S–S bond of intermediate **A** to form complex **B**; (iii) reductive elimination of copper(III) intermediate **B** to furnish desired thiocyanate **5** as well as copper(I) thiolate **C**; and (iv) regeneration of a molecule of disulfide **A** *via* the reaction of two molecules of copper(I) thiolate **C** under aerobic conditions.



Scheme 4. (a) Cu-mediated oxidative cyanation of thiophenols 4 reported by Castanheiro *et al*.; (b) The possible reaction mechanism for the formation of thiocyanates 5.

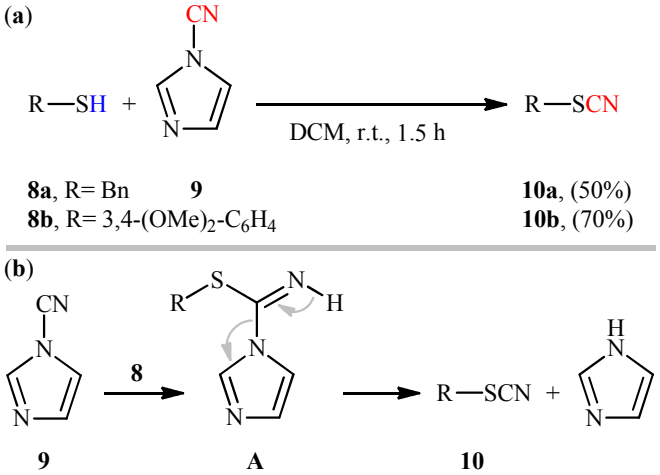
In 2014, Mizuno and colleagues reported a mild and fast metal-catalyzed direct cyanation of thiols with nucleophilic TMSCN using the combination of a 2 × 2 manganese oxide-based octahedral molecular sieve (OMS-2) and KF as the catalytic system in DMF under oxygen atmosphere [18]. Both aromatic and aliphatic thiols **6** undergo the cyanation process to generate the corresponding thiocyanates **7** in almost quantitative yields (Scheme 5). It should be mentioned that in the absence of nucleophilic catalyst (KI) the desired products were also obtained; albeit, in lower yields. Furthermore, the outcome of the reaction was strongly dependent on solvent. Polar solvents such as MeCN, THF, DMF, DMAc were found to be more effective than non-polar solvents such as chloroform, *n*-hexane and toluene. Very recently, Liu and Sun developed electrochemical version of this reaction under external oxidant- and transition-metal-free conditions [19].



Scheme 5. OMS-2/KF-catalyzed cyanation of thiols 6 with TMSCN.

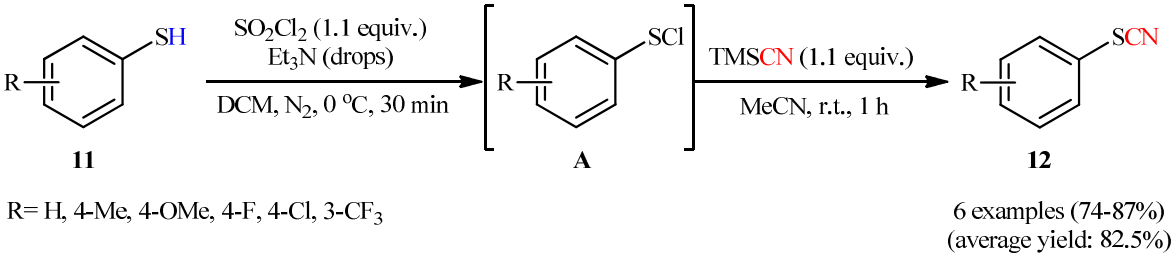
3. Metal-free reactions

Metal-free direct cyanation of thiols was accomplished first in 1976 by Wakselman *et al* [20]. The authors demonstrated that the S-cyanated derivative of cysteine could be successfully obtained in quantitative yield *via* the treatment of cysteine with 1-cyano-4-dimethylaminopyridium tetrafluoroborate (CDAP) under acidic conditions. Two decades later, Tam [21] and Pipes [22] successfully applied this strategy for cyanation of the thiol side chain of unprotected peptides. In 2000, Wu and co-workers disclosed the usefulness of 1-cyanoimidazole as efficient cyanating agent for direct metal-free cyanation of S-H bond under ambient conditions [23]. They showed that in the absence of any base or additive, reaction of thiols 8 with 1-cyanoimidazole 9 furnished the corresponding thiocyanates 10 within 1.5 h (Scheme 6a). However, in this preliminary work, only two examples were provided, without any substrate scope exploration. Notably, besides thiols, several other carbon and heteroatom nucleophiles were also successfully participated in this cyanation, such as amines, acetylenes, Grignard reagent and so on. According to the authors, this reaction proceeds through an addition-elimination process (Scheme 6b).



Scheme 6. (a) Miao-Tam's synthesis of thiocyanates 10; (b) proposed mechanism for the formation of thiocyanates 10.

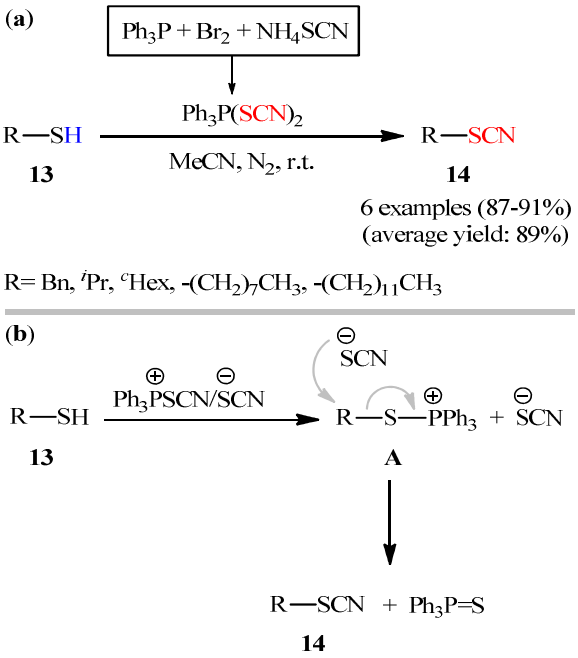
Drawing inspiration from these works, Still and Watson developed a two-step-one-pot S–H chlorination-cyanation procedure for the synthesis of thiocyanates from the corresponding thiols using SO_2Cl_2 and trimethylsilyl cyanide (TMSCN) as chlorinating and cyanating agents, respectively [24]. Thus, in the presence of a catalytic amount of Et_3N in DCM at 0 °C, the reaction of a series of aryl thiols 11 with SO_2Cl_2 furnished arenesulfenyl chloride intermediates A, which after treatment with TMSCN led rapidly to the formation of the corresponding aryl thiocyanates 12 in high yields. As shown in Scheme 7, both electron-donating and electron-deficient functionalities were tolerated well by this protocol. However, neither aliphatic nor benzylic thiols were examined in this synthetic strategy.



Scheme 7. One-pot two-step S–H chlorination-cyanation of aryl thiols 11.

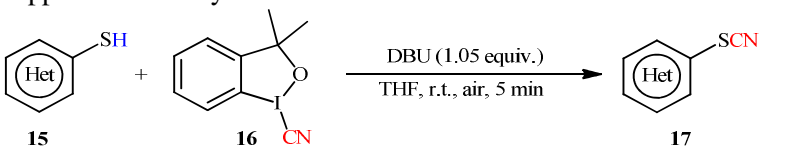
In 2002, Iranpoor and co-workers introduced the use of triphenyldithiocyanatophosphorane [$Ph_3P(SCN)_2$] as an efficient reagent for the direct cyanation of aliphatic thiols under catalyst-free conditions [25]. Thus, a panel of six aliphatic thiocyanates 14 were successfully prepared by treatment of the corresponding aliphatic thiols 13 with *in situ* generated $Ph_3P(SCN)_2$ (from the reaction between Ph_3P, Br_2, and NH_4SCN) in MeCN at

room temperature (Scheme 8a). Under the optimal conditions, primary thiols produced exclusively the corresponding thiocyanates, but secondary thiols gave small amounts of isothiocyanates as side products. Unfortunately, the scope of this reaction was not examined for aromatic thiols. A possible mechanism for this transformation was proposed by the authors, and is shown in Scheme 8b.



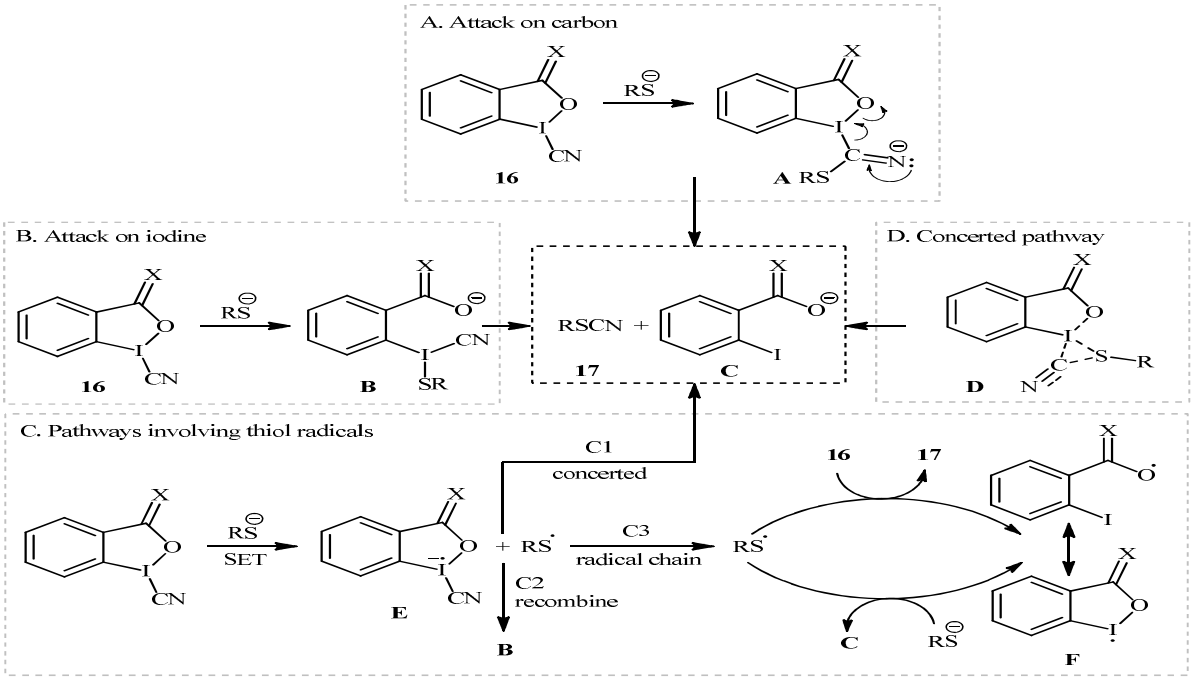
Scheme 8. (a) conversion of aliphatic thiols 13 to thiocyanates 14 by *in situ* generated $Ph_3P(SCN)_2$; (b) mechanistic explanation for the formation of thiocyanates 14.

With the aim of designing a general and practical protocol to thiocyanates through the catalyst-free direct cyanation of thiols, in 2015, Waser and co-worker were able to demonstrate that a divers range of functionalized (hetero)aromatic thiocyanates 17 could be obtained in good to excellent yields from the reaction of corresponding (hetero)aromatic thiols 15 with 1-cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxol 16 as a user friendly electrophilic cyanating agent, employing DBU as a base under ambient conditions (Scheme 9) [26]. The reaction is noteworthy in that a number of important functional groups (*e.g.*, OMe, SMe, OH, F, Cl, Br, CF_3, NH_2, NO_2, CO_2H, CO_2Me) we well tolerated, which are very useful for further manipulation of the end products. Furthermore, the process is applicable for cyanation of selenols, as exemplified by the formation of phenyl selenocyanate in excellent yield of 88% from phenylselenol. It is worthwhile to note that cyanation of aliphatic thiols was also achieved with use of similar reaction conditions, by only replacing 1-cyano-3,3-dimethyl-3-(1*H*)-1,2-benziodoxol with 1-cyano-1,2-benziodoxol-3-(1*H*)-one. Double and triple cyanation reactions of were also possible by using 1-cyano-1,2-benziodoxol-3-(1*H*)-one as cyanating agent, as demonstrated by the synthesis of bisthiocyanate and tristhiocyanate in 87 and 78%, respectively. As shown in Scheme 10, several pathways involving a thiolate or a thiyl radical as the nucleophile have been proposed by the authors for the reaction mechanism and validated by computational studies.



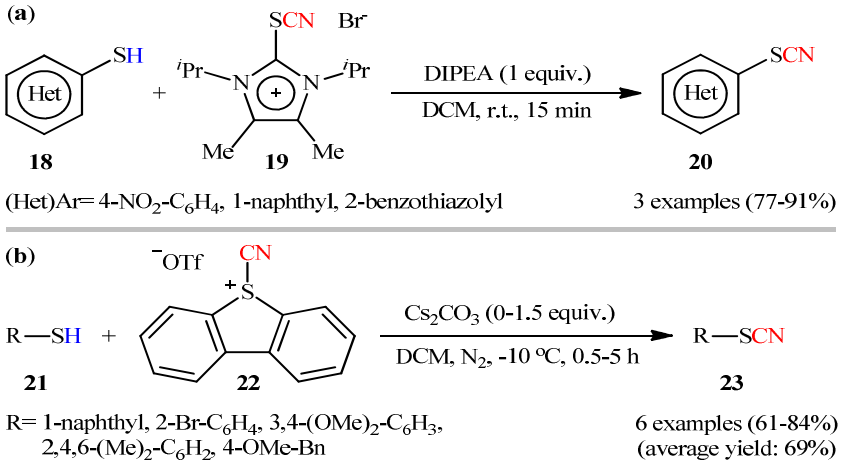
(Het)Ar= Ph, 4-tBu-C_6H_4, 4-SMe-C_6H_4, 4-CO_2H-C_6H_4, 4-CH_2CO_2H-C_6H_4, 4-F-C_6H_4, 4-CF_3-C_6H_4, 4-NO_2-C_6H_4, 4-NHAc-C_6H_4, 3-Me-C_6H_4, 3-OMe-C_6H_4, 3-OH-C_6H_4, 3-NH_2-C_6H_4, 2-Br-C_6H_4, 2-CO_2Me-C_6H_4, 2,5-Cl_2-C_6H_3, 2-naphthyl, 2-pyrimidyl, 2-benzothiazolyl

Scheme 9. Waser's synthesis of (hetero)aromatic thiocyanates 17.



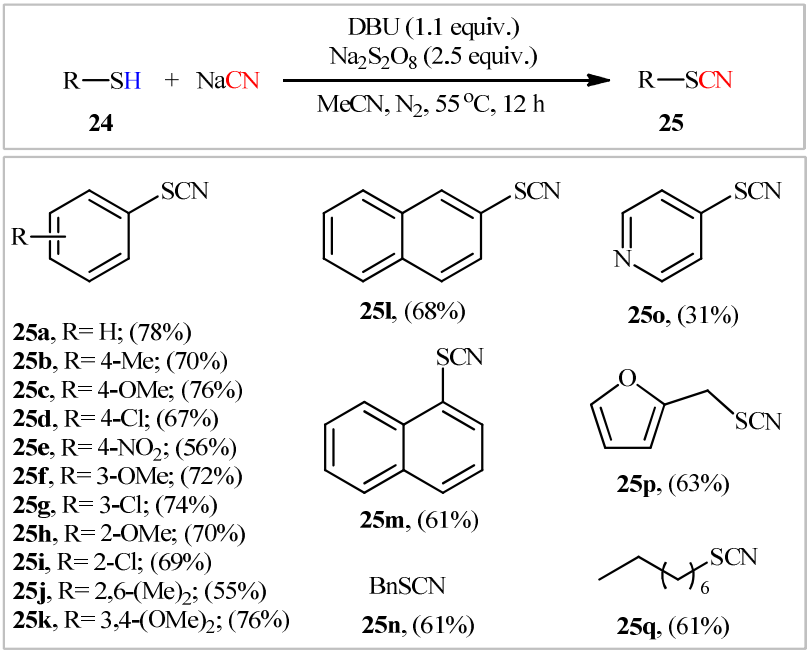
Scheme 10. Speculative mechanism pathways for the reaction in Scheme 9.

Concurrently, the group of Alcarazo developed an efficient protocol for the synthesis of (hetero)aromatic thiocyanates 20 *via* base-mediated direct cyanation of the respective (hetero)aromatic thiols 18 by using 2-thiocyanoimidazolium salt 19 as a novel electrophilic cyanating agent (Scheme 11a) [27]. The best conversion efficiency was obtained for the reactions containing 1.0 equiv. of *N,N*-diisopropylethylamine (DIPEA) in DCM at room temperature. The standard condition was also successfully applied to the synthesis of cyanamides through the cyanation of corresponding amines. Recently, the same research group prepared a super electrophilic cyanating reagent, 5-(cyano)dibenzothiophenium triflate 22, by activation of easily available dibenzo[*b,d*]thiophene-5-oxide with Tf_2O and subsequent reaction with TMSCN [28]. They showed that treatment of various thiols 21 with the newly developed cyanation reagent 22 in the presence of Cs_2CO_3 in DCM provided the corresponding thiocyanates 23 in high yields (Scheme 11b). Although both aromatic and aliphatic were well tolerated under the reaction conditions, limited scope of substrates was demonstrated. Notably, aromatic thiols did not require the addition of base to afford the thiocyanates and only in the case of aliphatic substrates base was used.

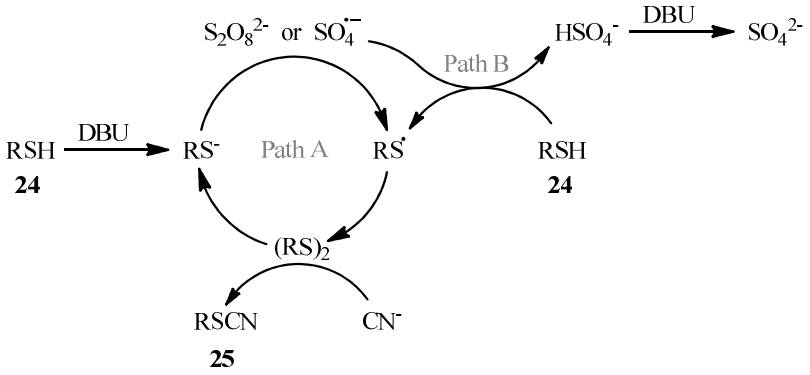


Scheme 11. (a) DIPEA-mediated *S*-cyanation of thiols 18 with 2-thiocyanoimidazolium salt 19; (b) oxidative cyanation of thiols 21 with 5-(cyano)dibenzothiophenium triflate 22.

An interesting contribution to this research arena was reported by Wujiong *et al* in 2017 [29]. They disclosed that treatment of various aliphatic, benzylic, and aromatic thiols 24 with NaCN in the presence of a combination of DBU and $K_2S_2O_8$ in MeCN under an inert atmpsphere afforded the corresponding thiocyanates 25 in fair to high yields (Scheme 12). The result demonstrated that heteroaromatic thiols afforded relatively lower yield compared to the aliphatic and aromatic thiols. Interestingly, the outcome of reaction almost was not dependent on the electronic steric effects of the substituents on phenyl ring periphery of aromatic thiols. Therefore, a series of important functional groups (e.g., OMe, Cl, NO_2) at different positions of phenyl rings of aromatic thiols were well tolerated by this reaction, thus indicating its broad applicability. According to the authors proposed mechanism (Scheme 13), this S-C bond formation reaction most likely proceeds *via* a radical pathway.



Scheme 12. Wujiong's synthesis of thiocyanates 25.

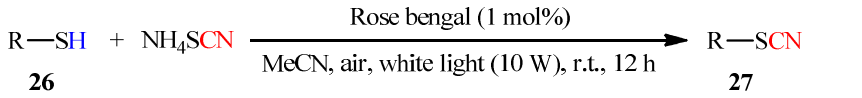


Scheme 13. Suggested mechanism for the generation of thiocyanates 25.

4. Photocatalyzed reactions

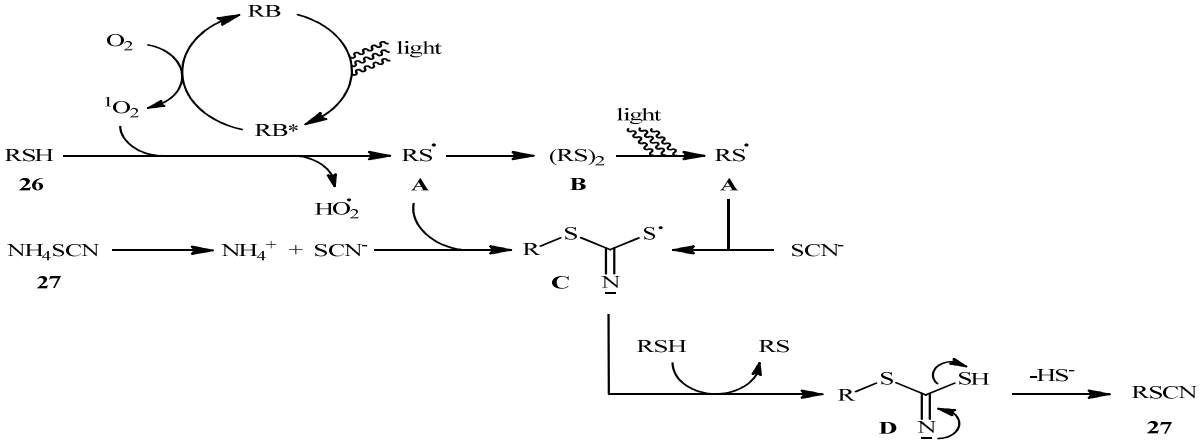
In 2018, Guo and co-workers communicated the first and only example of direct synthesis of thiocyanates from thiol derivatives through photocatalytic S–H bond cyanation [30]. By employing 4-methylbenzenethiol and ammonium thiocyanate (NH_4SCN) as the model substrates, the reaction variables such as photocatalyst and solvent were carefully studied. The best conversion efficiency (85% isolated yield) was obtained for the reaction performed in the presence of a catalytic amount of Rose bengal (an organic dye) in MeCN under irradiation of white light (10W) at room temperature. Notably, by substituting NH_4SCN with KSCN the desired thiocyanate was also abstained, albeit at lower yield

(70%). Under the optimized condition, various aromatic, heteroatomatic, benzylic and aliphatic thiols 26 reacted well and afforded the corresponding thiocyanates 27 in fair to high yields (Scheme 14). The reaction is noteworthy in that a divers range of sensitive functional groups (e.g., F, Cl, Br, OMe, OH, NH_2, NO_2, CO_2Me) we well tolerated, which might provide potential opportunities for further functionalization of the end products. Furthermore, the reaction could also be easily scaled up to the gram-scale as exemplified by the formation of (2-thiocyanatoethyl)benzene on a 0.73 scale (62%). Interestingly, this approach was also suitable for selenols as exemplified by the synthesis of selenocyanatobenzene (21%). Based on a series of control experiments and the literature, the authors proposed that this reaction proceeds through the following key steps (Scheme 15): (1) excitation of Rose bengal (RB) under the irradiation of visible light to its excited state species (RB*); (2) interaction of RB* with O_2 to afford $^1O_2$ and regenerates its ground state (RB) *via* the energy transfer; (3) trapping of a hydrogen atom from thiol affords the thioyl radical A; (4) radical coupling of thioyl A to form disulfide intermediate B; (5) homolytic dissociation of B to regenerate radical A; (6) coupling of thioyl radical A with SCN^- to form the intermediate C; (7) trapping of the intermediate C with another thiol results in propagation and formation of the intermediate D; and (8) release of HS^- from intermediate D to produce the desired product 27.



R= 4-Me-C_6H_4, 4-^{i}Pr-C_6H_4, 4-^{t}Bu-C_6H_4, 4-OMe-C_6H_4, 4-NH_2-C_6H_4, 4-OH-C_6H_4, 4-NHCOMe-C_6H_4, 4-NO_2-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 3-Me-C_6H_4, 3-OMe-C_6H_4, 3-Cl-C_6H_4, 2-CO_2Me-C_6H_4, 3,4-Me_2-C_6H_3, 3,4-$(OMe)_2$-C_6H_3, 3,5-Me_2-C_6H_3, 3,5-$(OMe)_2$-C_6H_3, 2,4-$(Cl)_2$-C_6H_3, 2-Cl-4-F-C_6H_3, 1-naphthyl, 2-naphthyl, Bn, 4-^{t}Bu-Bn, 4-OMe-Bn, 4-Cl-Bn, 2-Cl-Bn, 2-Br-Bn, -CH_2CH_2Ph, 2-benzothiazolyl, 2-1,3,4-thiadiazolyl, 5-Cl-2-1,3,4-thiadiazolyl, 4-Me-7-2*H*-chromen-2-onyl

Scheme 14. Direct photocatalytic S-cyanation of thiols 26 with NH_4SCN.



Scheme 15. Plausible reaction mechanism for the formation of thiocyanates 27.

5. Conclusion

As one of the prominent medicinal motifs, the thiocyanate group featured in a large number of bioactive compounds and natural products. Moreover, organic thiocyanates frequently serve as precursors for the synthesis of various important organosulfur compounds such as thiols, disulfides, thioethers, thioesters, trifluoromethyl thioethers, S-thiocarbamates, and sulfonyl cyanides. Therefore, there is continuing interest in the development of practical and efficient synthetic methodologies for their preparation. In this regards, synthesis of organic thiocyanates through the direct cyanation of corresponding thiols have witnessed rapid and comprehensive development in recent years. As illustrated, the major advantages of this page of thiocyanate synthesis include the use of simple and easily

available starting materials, and its high atom and step economy. Hopefully, this synthetic strategy will be employed in the preparation of biologically important and natural thiocyanate compounds in future studies.

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