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Recent advances in the synthesis of α-thiocyanatoketones and β-thiocyanato alcohols through the direct oxy-/hydroxy-thiocyanation of unsaturated hydrocarbons

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ABSTRACT

The objective of the present review is to give an overview on recent advances on the synthesis of α-thiocyanatoketones and β-thiocyanato alcohols through the direct oxy-/hydroxy-thiocyanation reactions of unsaturated hydrocarbons. The literature has been surveyed up until the end of October 2024. We hope that this review will inspire the development of novel thiocyanative difunctionalization reactions and improve the efficiency of existing ones.

1. Introduction

Organosulfur compounds are a special class of organic substances that contain at least one carbon-sulfur bond [1-3]. These compounds are ubiquitous in natural products [4], pharmaceuticals [5], agrochemicals [6], and functional materials [7]. Organic thiocyanates (R-SCN) are an important subclass of organosulfur compounds which not only occur as key functionalities in various biologically important natural products (Scheme 1) [8-10], but also serve as versatile building blocks for the concise synthesis of various sulfur-containing functional groups (e.g., trifluoromethylthiol, sulfoxide, S-argio carbamothioate) [11-13] and scaffolds (e.g., thiazoles, thiazinones, 5-sulfenyl tetrazoles) [14-16]. The widespreat imprtance of organic thiocyanates in various fields has triggered considerable interest in developing new methods for their synthesis. Alkenes and alkynes are inexpensive, widely available feedstocks that serve as synthons for a vast array of chemical transformations [17]. Within the realm of alkenes and alkynes chemistry, the direct vicinal difunctionalization reactions have attracted significant attention from synthetic chemists because such reactions allow direct construction of complex molecules from simple, organic feedstock chemicals, within a single click [18]. The oxidative difunctional of alkenes or alkynes to access difunctional ketone or alcohol derivatives is of significant interest to organic chemists [19]. In this regard, the direct (hydr)oxy-thiocyanation reactions have become a powerful tool to achieve synthetically important α-oxothiocyanates and β-thiocyanato alcohols under benign conditions (Figure 1). Recently, Zhao and co-workers published an interesting review paper that highlights the advances on the direct thiocyanation reactions [20]. However, synthesis of α-thiocyanatoketones and β-thiocyanato alcohols through the direct oxy- and hydroxy-thiocyanation reactions of unsaturated compounds was almost omitted. The aim of

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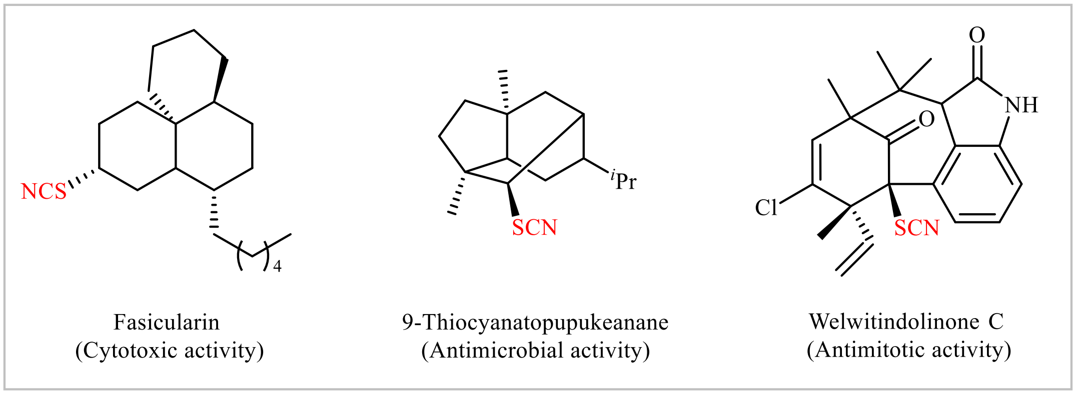


Scheme 1. Selected examples of SCN-containing biologically active natural products.

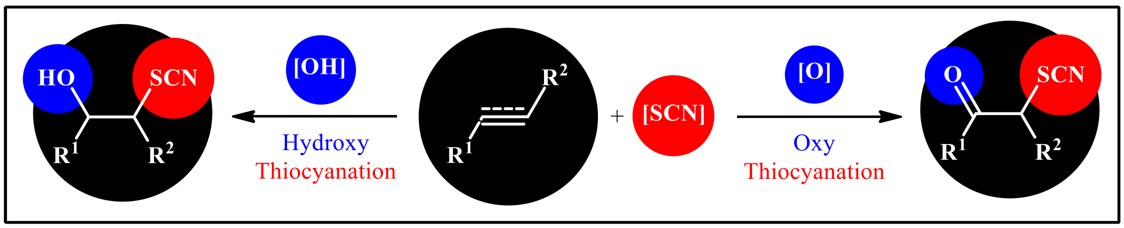
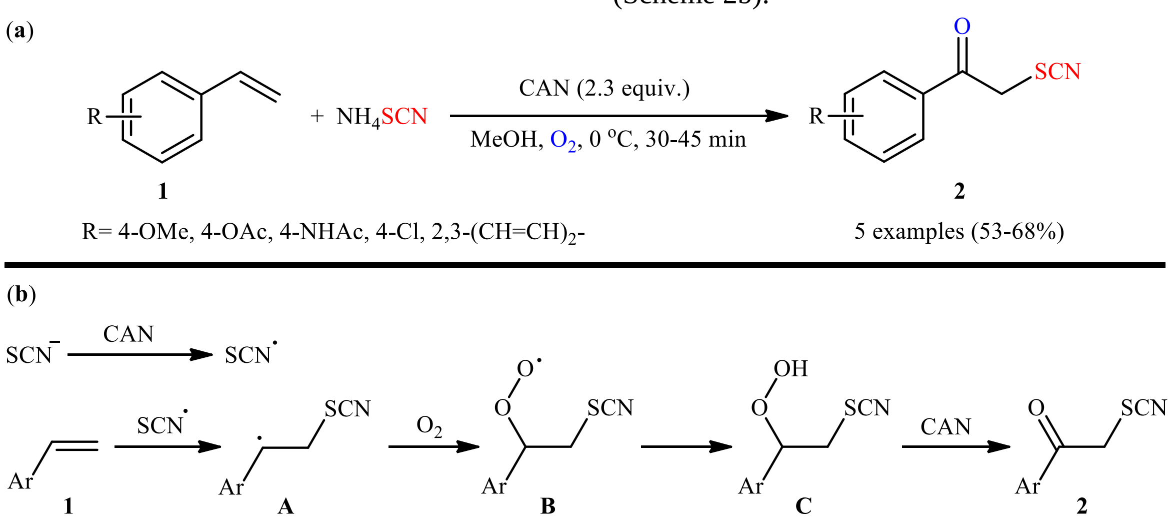


Fig. 1. Direct oxy-/hydroxy-thiocyanation of unsaturated hydrocarbons.

this work is to present a comprehensive overview of the direct (hydr)oxy-thiocyanation of alkene and alkyne substrates with particular emphasize on the mechanistic aspect of reactions.

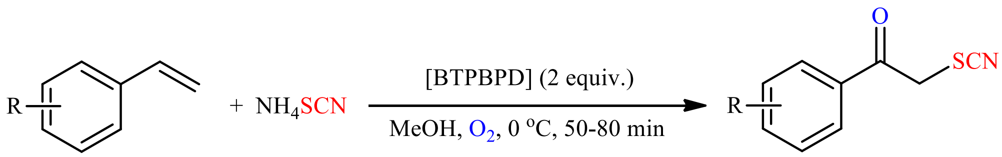
2. Oxy-thiocyanation of alkenes

In 2000, Nair and co-workers reported one of the earliest example of the direct oxy-thiocyanation of alkenes **1** using ammonium thiocyanate (NH_4SCN) as the source of thiocyanato group under an oxygen atmosphere [21]. The reactions were carried out in the presence of over-stoichiometric amounts of cerium(IV) ammonium nitrate (CAN) in MeOH, completed within 30-45 min at room temperature, and selectively afforded the corresponding phenacyl thiocyanates **2** in moderate to high yields (Scheme 1a). The authors evoked a reaction mechanism initiated by single electron oxidation of SCN^- by CAN to yield the corresponding radical. Next, the thiocyanato radical selectively attacks the less hindered end of alkene **1** to form the benzylic radical **A** that, after trapping of oxygen affords the peroxy radical **B**. Subsequently, the newly generated radical abstracts a hydrogen from the solvent to form the hydroperoxide **C**. Finally, oxidative cleavage of **C** by CAN affords the observed product **2** (Scheme 2b).



Scheme 2. (a) Nair's synthesis of α-thiocyanato ketones **2**; (b) mechanistic explanation for the formation of α-thiocyanato ketones **2**.

Twelve years later, a similar difunctionalization strategy was reported by Badri and Gorjizadeh using *cis*-1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate (BTPBPD) as an efficient and inexpensive oxidizing agent [22]. As shown in Scheme 3, eight phenacyl thiocyanate derivatives **4** were efficiently produced from the corresponding styrenes **3** under mild conditions using methanol as solvent. Although a series of styrene derivatives bearing both electron-donating (*e.g.*, Me, OMe) and electron-withdrawing (*e.g.*, NO_2, F, Cl, Br, CO_2H) functional groups were well tolerated under the reaction conditions, the applicability of aliphatic and internal alkenes was not investigated under the conditions employed.

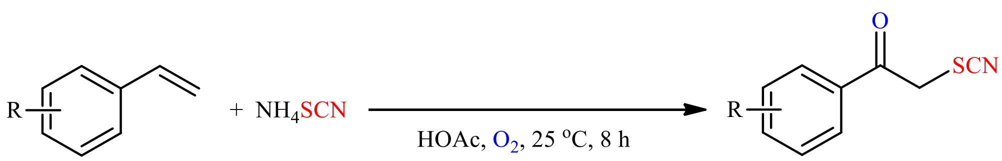


3 **4**

R= H, 4-Me, 4-OMe, 4-F, 4-Cl, 4-Br, 4-CO_2H, 4-NO_2 8 examples (65-92%)

Scheme 3. Badri-Gorjizadeh's synthesis of α-thiocyanato ketones **4**.

In 2015, Pan and Zou along with their co-workers were able to demonstrate that molecular oxygen can efficiently induce free radical oxy-thiocyanation of alkenes leading to α-oxothiocyanates [23]. Thus, a variety of α-thiocyanato ketones **6** were synthesized by treatment of styrene derivatives **5** with NH_4SCN in the absence of any external oxidant in HOAc at room temperature under an oxygen atmosphere (Scheme 4). The results indicated that the outcome of this reaction is highly dependent on the electronic and steric effects of the substituents on the aromatic units. In general, electron-rich styrenes (except OMe-substituted derivatives) were high yielding compared to electron-poor ones and *para*-substituted styrenes gave higher yields than either *ortho*- or *meta*-substituted ones. Unfortunately, OMe-, CN-, and NO_2-substituted styrene derivatives were quite inert under the identical conditions. Furthermore, the process was not applicable for oxy-thiocyanation of α- or β-substituted styrenes and non-conjugated terminal alkenes.



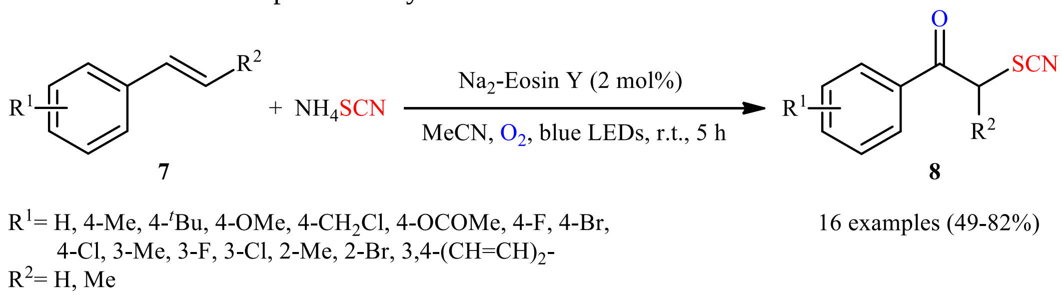
5 **6**

R= H, 4-Me, 4-OCOMe, 4-F, 4-Cl, 4-Br, 3-Me, 3-F, 3-Cl, 3-CF_3, 2-Me, 2-F, 2-Cl 13 examples (16-80%)

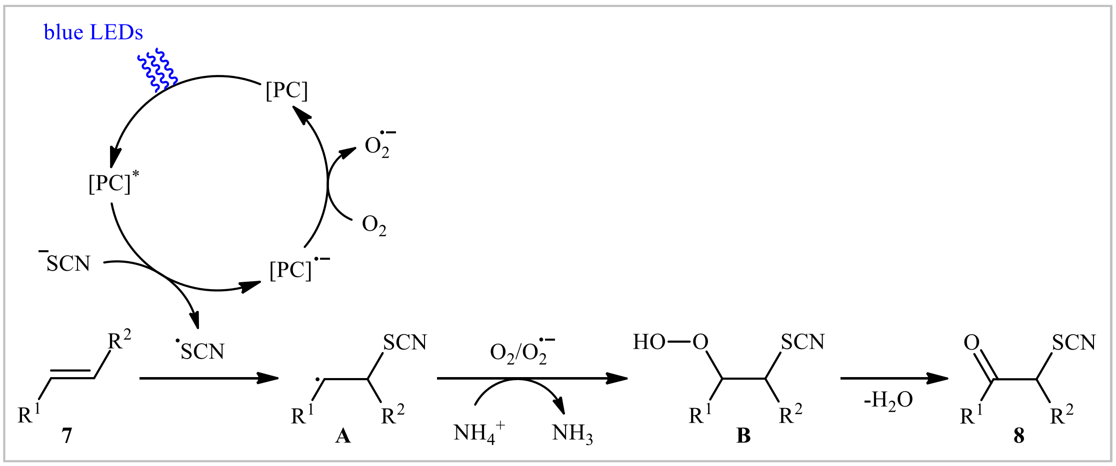
Scheme 4. Pan-Zou's synthesis of α-thiocyanato ketones **6**.

Subsequently, photocatalyzed version of this oxidative difunctionalization reaction was disclosed by Nan and Yue [24], who revealed that the treatment of various styrenes **7** bearing electron-deficient (F, Cl, Br, OCOMe) and electron-donating groups (Me, OMe, ^{t}Bu) with NH_4SCN in the presence of a catalytic amount of Na_2-Eosin Y in MeCN under the irradiation of 3W blue LED under an oxygen atmosphere at room temperature, afforded the corresponding α-thiocyanato ketones **8** in moderate to good yields, ranging from 49% to 82% (Scheme 5). Although the electronic effect was not strong like previous works, the reaction still works better with electron rich than with electron rich substituents on the phenyl ring periphery of styrenes. On the other hand, no steric effect was observed for styrene isomers with methyl group at *ortho*, *meta* and *para* positions. Nevertheless, none of the desired products were detected when stilbene and an aliphatic alkene such as hex-1-ene were employed in this reaction system. Regarding the reaction mechanism, based on some control experiments, the authors proposed the following reaction pathways (Scheme 6): (i) photoexcitation of the ground state Na_2-Eosin Y by visible light to generate the excited state Na_2-Eosin Y*; (ii) single-electron transfer (SET) from thiocyanate anion to Na_2-Eosin Y* to produce thiocyanate radical and Na_2-Eosin $Y^{\bullet-}$, which immediately undergoes oxidation by dioxygen to form the ground-state Na_2-Eosin Y and $O_2^{\bullet-}$; (iii) electrophilic addition of the $SCN^{\bullet}$ to alkene **7** to produce the alkyl radical **A**; (iv) interaction of radical intermediate **A** with $O_2^{\bullet-}$ or O_2 and NH_4^+ to give hydroperoxide intermediate **B**; and (v) elimination of water from intermediate **B** to yield the final product **8**.

Shortly afterwards, Chen's research group disclosed that *N*-thiocyano-dibenzenesulfonimide [$PhSO_2N(SCN)SO_2$ Ph] can be used as an efficient electrophilic thiocyanation reagent in oxy-thiocyanation of alkene substrates when alcohols were used as oxygenating agents [25].

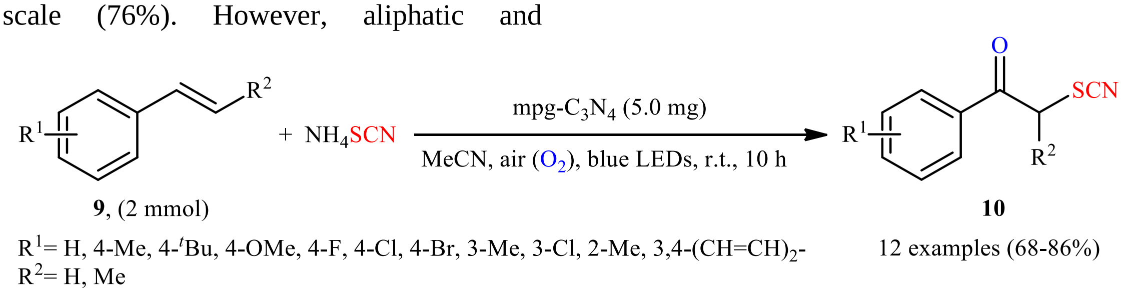


Scheme 5. Nan-Yue's synthesis of α-thiocyanato ketones **8**.



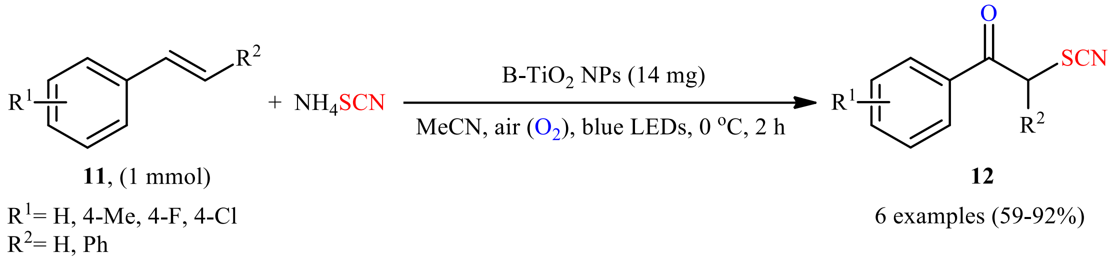
Scheme 6. Mechanism that accounts for the formation of α-thiocyanato ketones **8**.

In 2021, Peng and co-workers reported the use of mesoporous graphitic carbon nitride (mpg-C_3N_4) as a metal-free heterogeneous photocatalyst for regioselective oxy-thiocyanation of styrene derivatives **9** with NH_4SCN under the irradiation of 18 W blue LEDs [26]. The reactions were implemented under an air atmosphere without any additional oxidant at room temperature, tolerated a series of important functional groups (*e.g.*, OMe, F, Cl, Br), and afforded the target 1-aryl-2-thiocyanatoethanones **10** in good to high yields (Scheme 7). Notably, the protocol was also applicable for gram-scale synthesis of α-thiocyanato ketones as exemplified by the formation of 1-phenyl-2-thiocyanatoethanone on a 1.35 g scale (76%). However, aliphatic and heteroaromatic terminal alkenes as well as 1,2-diaryl-substituted alkenes did not respond to the reaction under standard conditions. The recycling test established that the catalyst could be easily separated from the reaction mixture by centrifugation and reused in several consecutive trials without significant loss of its activity (from 86% in the first run to 78% in the sixth run). The radical and active species trapping experiments with the commonly used scavengers 2,2,6,6-tetramethylpiperidinooxy (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT), *p*-benzoquinone (BQ), carotene, ammonium oxalate (AO) and *tert*-butanol pointed toward a radical reaction mechanism.



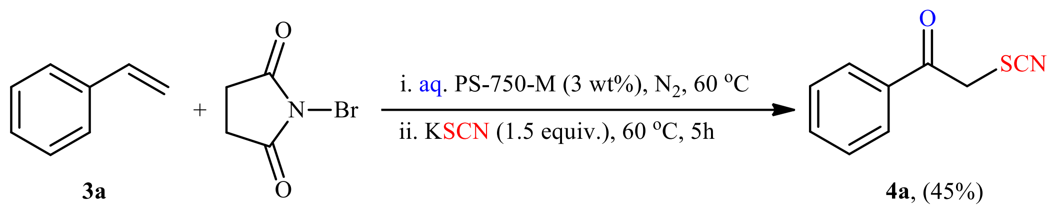
Scheme 7. Peng's synthesis of α-thiocyanato ketones **10**.

Concurrently, Sarvari and Valikhani prepared boron-doped TiO_2 nanoparticles (B-TiO_2 NPs) with B/Ti molar ratio 1/10 through a sol–gel process using boric acid and titanium (IV) butoxide [27]. The crystal size of prepared material was about 15 nm and exhibited a large surface area of over 119 m^2g^{-1}. The authors demonstrated that this heterogeneous catalyst can effectively promote oxy-thiocyanation of various aromatic alkenes **11** (styrene and stilbene derivatives) with NH_4SCN at 0 °C under the open air to furnish the corresponding α-thiocyanato ketones **12** in moderate to excellent yields (Scheme 8). In a similar manner, oxy-thiocyanation of alkyne substrates gave the respective α-thiocyanato ketones in good yields. Using the same scenario, this research group was able to synthesis two α-thiocyanato ketones from the corresponding alkynes. Noteworthy, the catalyst could be reused for six reaction runs with only slight loss of the catalytic activity. The authors proposed mechanism for this reaction is analogous to the one depicted in Scheme 6 for Na_2-Eosin-catalyzed oxy-thiocyanations.



Scheme 8. Sarvari's synthesis of α-thiocyanato ketones **12**.

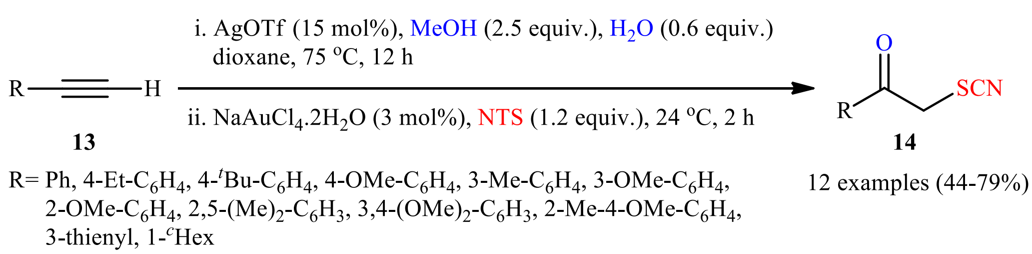
Along this line, in 2021, Handa and co-workers reported an example of α-thiocyanato ketone synthesis from the corresponding alkene in the most environmentally benign solvent, water, under mild conditions [28]. They showed that unsubstituted styrene **3a** underwent oxy-bromination with *N*-bromo succinimide (NBS) in 3 wt% aq. PS-750-M to afford the corresponding α-bromo ketone, which after treatment with KSCN resulted in the formation of 1-phenyl-2-thiocyanatoethanone **4a** in 45% yield (Scheme 9).



Scheme 9. Handa's synthesis of α-thiocyanato ketones **4a**.

3. Oxy-thiocyanation of alkynes

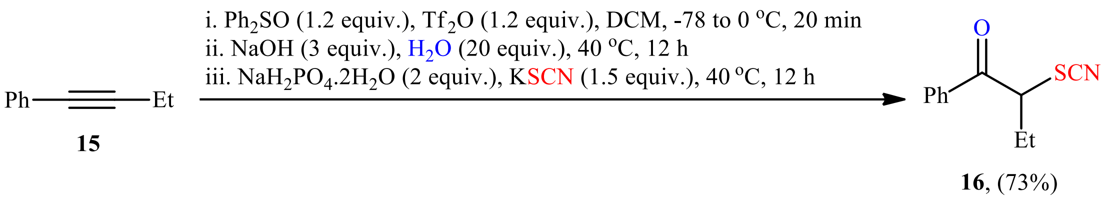
In 2018, See and Zhao described a beautiful Ag/Au-catalyzed one-pot two-step protocol for the direct oxy-thiocyanation of terminal alkynes to deliver corresponding α-thiocyanato ketones [29]. In the first step, Ag-catalyzed hydration of alkynes **13** in the presence of a mixture of MeOH and water resulted in the formation of corresponding acetophenones, and in the second step, the treatment of resulted acetophenones with *N*-thiocyanosuccinimide (NTS) as an electrophilic thiocyanating reagent in the presence of a catalytic amount of $NaAuCl_4$ furnished the expected α-thiocyanato ketones **14** in moderate to good yields within 2 h (Scheme 10). A variety of electron-rich aromatic and vinylic alkynes were successfully used, including heteroaryl alkynes. However,



Scheme 10. See-Zhao's synthesis of α-thiocyanato ketones **14**.

the reaction of halogen-substituted aryl alkynes resulted in a messy mixture and applicability of electron-poor aromatic terminal alkynes as starting materials was not investigated in this study.

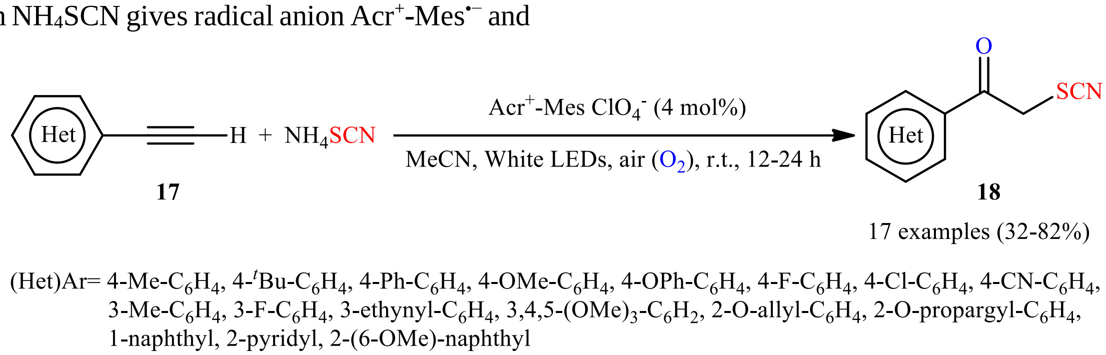
Subsequently, an example of an α-alkyl-substituted α-thiocyanato ketone **16** syntheses was reported by Li and co-workers through sulfur-mediated oxy-thiocyanation of corresponding internal alkyne **15** *via* a one-pot three-step sequential process (Scheme 11) [30]. The reaction initiated with the interaction of alkyne **15** with triflic anhydride (Tf_2O) activated diphenyl sulfoxide (Ph_2SO) to give a sulfonium vinyl triflate intermediate, followed by a subsequent hydrolysis to give an α-sulfonium ketone, and then substitution with KSCN.



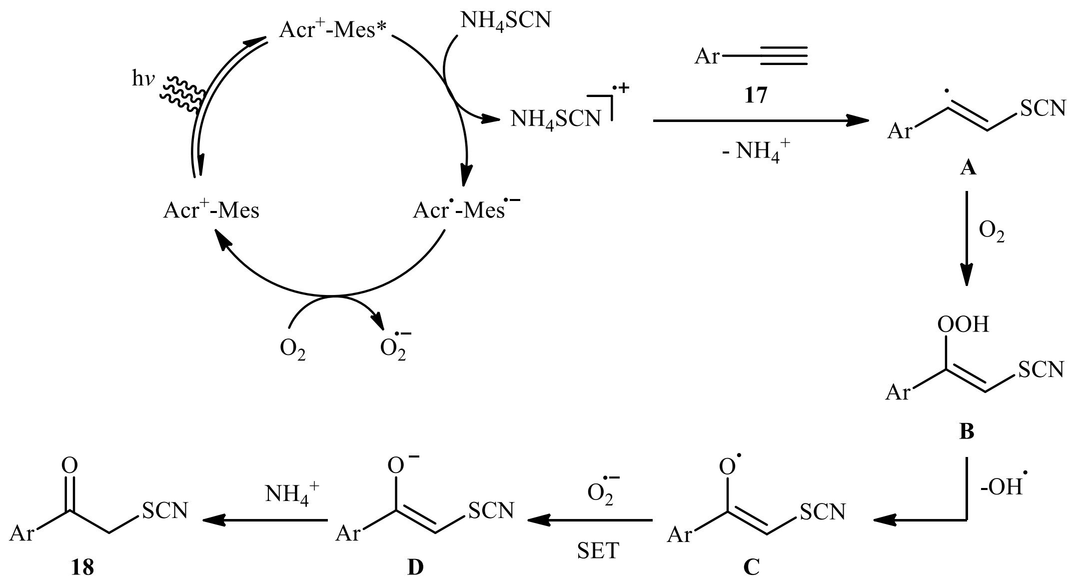
Scheme 11. Li's synthesis of α-thiocyanato ketone **16**.

Concurrently, Kumaraswamy and Vijaykumar reported their results on the visible-light induced direct oxy-thiocyanation of various (hetero)aromatic terminal alkynes **17** with NH_4SCN using 9-mesityl-10-methylacridiniumperchlorate (Acr^+-Mes ClO_4^-) as an electron transfer photo-catalyst [31]. Optimal conditions for this photoreaction were the use of household white 7W LED bulb as the light source, and MeCN as the solvent. The reaction proceeded cleanly at room temperature under open air and the desired α-thiocyanato ketones **18** were obtained in fair to high yields (Scheme 12). Regarding the influence of the substituents, phenylacetylene derivatives bearing an electron-donating group gave higher yields than those with an electron-withdrawing group. Unfortunately, alkyl, and alkenyl terminal alkynes as well as internal alkynes were insufficiently reactive under the standard conditions. The authors assume that the mechanistic pathway of this transformation involves the initial formation of singlet excited-state Acr^+-Mes^* *via* the excitation of photocatalyst (Acr^+-Mes) under light irradiation, which after quenching *via* single electron transfer from NH_4SCN gives radical anion Acr^+-$Mes^{\bullet-}$ and radical cation $NH_4SCN^{\bullet+}$. Next, radical addition of $NH_4SCN^{\bullet+}$ to terminal triple bond of alkyne **17** leads to alkene radical **A**, which after oxidation by air (O_2) followed by protonation (from NH_4^+) results in vinyl hydro-peroxide **B**. Meanwhile, Acr^+-$Mes^{\bullet-}$ undergoes oxidation with air (O_2) enabling the photo-catalyst reconstitution along with the formation of oxygen radical anion ($O_2^{\bullet-}$). Subsequently, a homolytic cleavage of hydro-peroxide **B** produces oxy-radical **C** with concomitant release of hydrogen peroxide. Finally, reduction of **C** by superoxide ($O_2^{\bullet-}$) *via* SET, ensuing protonation (from NH_4^+) results the observed product **18** (Scheme 13).

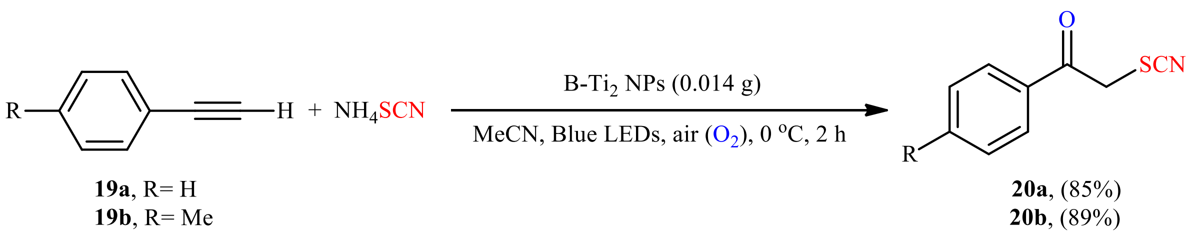
In 2021, in the same paper describing the direct of oxy-thiocyanation of styrene derivatives to α-thiocyanato ketones in the presence of boron-doped TiO_2 nanoparticle (B-TiO_2 NPs) as a heterogeneous photocatalyst under irradiation by visible light [27], Sarvari and Valikhani reported the successful preparation of α-thiocyanato ketones **20** through the reaction of terminal alkynes **19** with NH_4SCN under the identical conditions (Scheme 14).



Scheme 12. Synthesis of α-thiocyanato ketone **18** reported by Kumaraswamy and Vijaykumar.

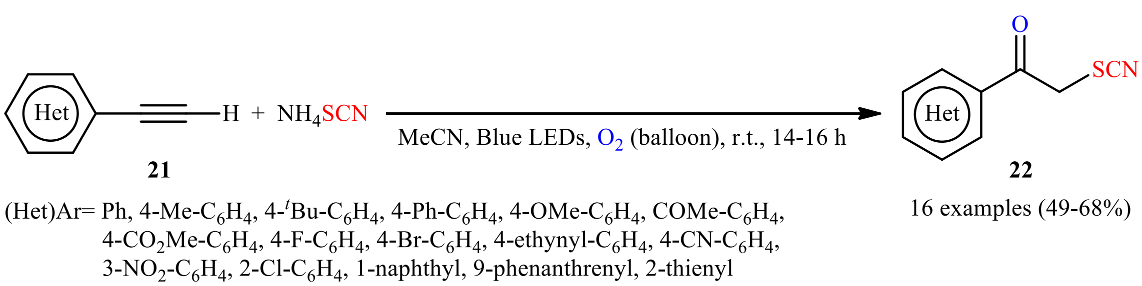


Scheme 13. Plausible mechanism for reaction in Scheme 12.

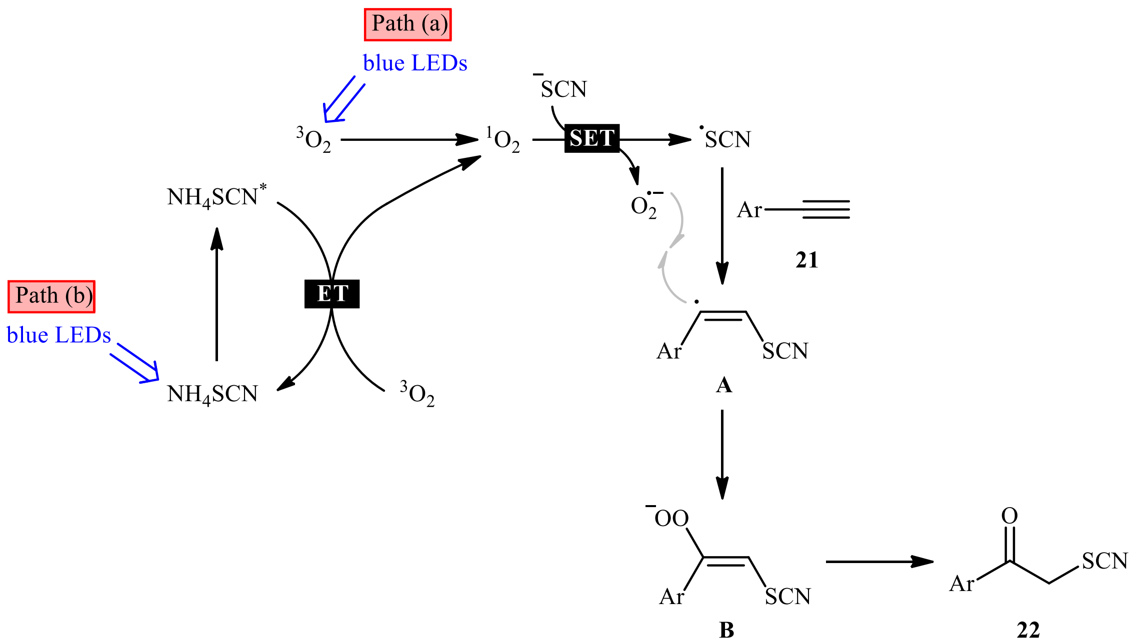


Scheme 14. Sarvari's synthesis of α-thiocyanato ketones **20**.

Very recently, Charpe-Hwang and co-workers demonstrated an innovative singlet oxygen ($^1O_2$)-mediated oxy-thiocyanation of terminal alkynes under visible light irradiation at room temperature [32]. Thus, a library of α-thiocyanato ketones **22** were synthesized in moderate to good yields *via* the treatment of corresponding phenylacetylene derivatives **21** with NH_4SCN and O_2 under visible light irradiation in the absence of any metal- and photo-catalyst (Scheme 15). A relatively wide panel of sensitive functional groups (*e.g.*, OMe, COMe, CO_2Me, F, Cl, Br, CN, NO_2) at different positions of phenyl rings of phenylacetylenes were well tolerated by this reaction, thus indicating its broad applicability. Importantly, the authors successfully applied their methodology as the key strategic step in synthesis of a series of pharmaceutically active compounds. Mechanistic investigation revealed that the reaction follows a SET pathway as depicted in Scheme 16.



Scheme 15. Charpe-Hwang's synthesis of α-thiocyanato ketones **22**.

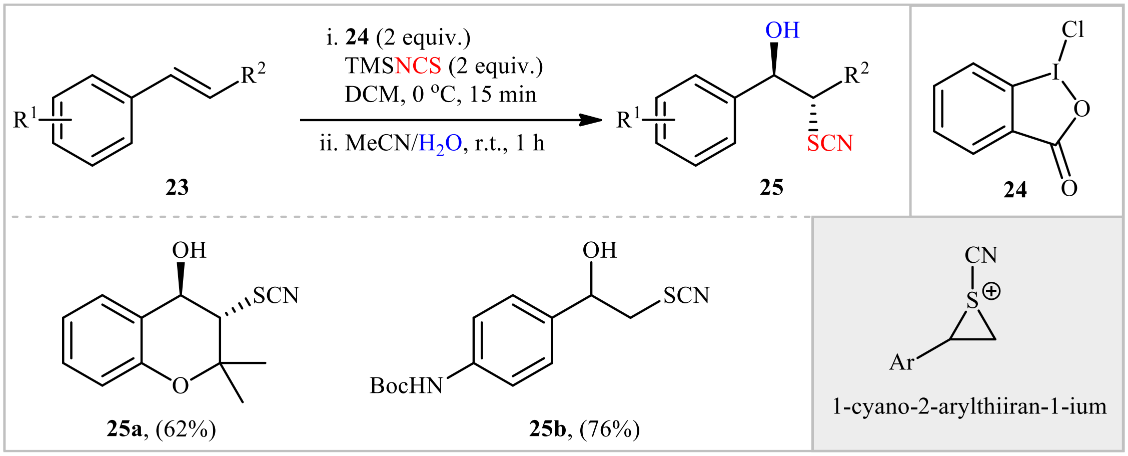


Scheme 16. Mechanism proposed to explain the formation of α-thiocyanato ketones **22**.

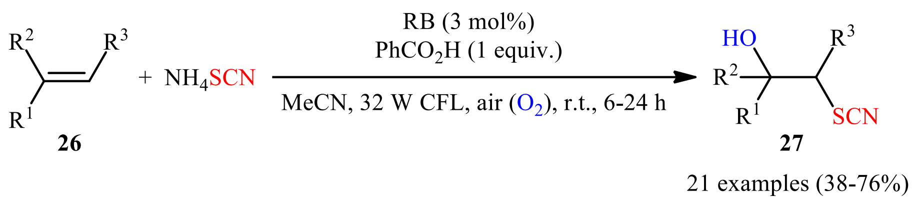
4. Hydroxy-thiocyanation of alkenes

Compared to direct oxy-thiocyanation of alkenes, the corresponding hydroxy-thiocyanation reactions has been much less developed [33, 34]. To the best of our knowledge, the first direct hydroxy-thiocyanation of alkenes was published in 2016 by Egami *et al*. [35], who showed that treatment of various styrene derivatives **23** with 1-chloro-1,2-benziodoxol-3-(1*H*)-one **24** and (trimethylsilyl)isothiocyanate (TMSNCS) in DCM at 0 °C resulted in the formation of corresponding β-thiocyanato alcohols **25** in good yields after hydrolysis (Scheme 17). Although only two examples were disclosed, as mentioned above, this paper represents the first example of direct hydroxy-thiocyanation of alkenes into β-thiocyanato alcohols and may serve as an inspiration for further researchers. Mechanistically, the authors suggested that 1-cyano-2-arylthiiran-1-ium might be the key intermediate for this hydroxy-thiocyanation reaction.

In 2018, Guan's research group disclosed a related hydroxy-thiocyanation of alkenes **26** using NH_4SCN as an SCN source under ambient visible light irradiation conditions which exhibited considerably better substrate scope when compared to the previous works [36]. The transformation was performed in the presence of commercially available inexpensive organic dye Rose Bengal (RB) as a photocatalyst and benzoic acid as an additive under irradiation of a 32W compact fluorescent lamp (CFL) at room temperature, which afforded β-thiocyanato alcohols **27** in moderate to good yields, ranging from 38% to 76% (Scheme 18). Various aromatic and heteroaromatic terminal alkenes were used to establish the general applicability of the method. In addition, a tolerance for 2,3-dimethylbuta-1,3-diene was also demonstrated. It is worthy of note that non-terminal and cyclic styrene derivatives could also be successfully converted into the desirable products under the conditions employed. However, when strong electron-donating group substituted α-methylstyrenes [*e.g.*, 2-(prop-1-en-2-yl)aniline] were employed under the optimal reaction conditions, only benzene ring substituted thiocyanation

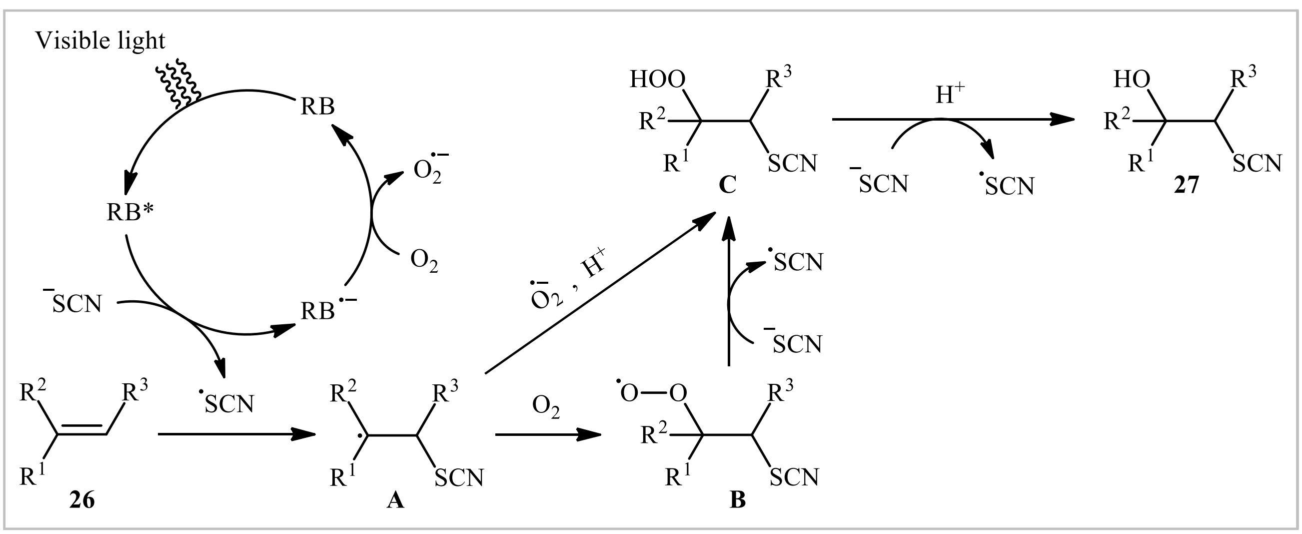


Scheme 17. Egami's synthesis of β-thiocyanato alcohols **25**.



R^1= Ph, 4-Me-C_6H_4, 4-Ph-C_6H_4, 4-OMe-C_6H_4, 4-Cl-C_6H_4, 4-F-C_6H_4, 4-Br-C_6H_4, 4-I-C_6H_4, 4-NO_2-C_6H_4, 3-Cl-C_6H_4, 2-OMe-C_6H_4, 1-naphthyl, 2-naphthyl, -C(Me)=CH_2
R^2= H, Me, Et, Ph
R^3= H, Me
R^2 + R^3= -$(CH_2)_4$-

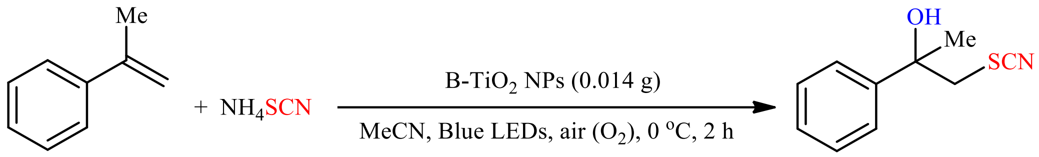
Scheme 18. Guan's synthesis of β-thiocyanato alcohols **27**.



Scheme 19. Mechanistic explanation for the formation of β-thiocyanato alcohols **27**.

products was obtained in poor yields. The authors proposed mechanistic pathway for this hydroxy-thiocyanation reaction is depicted in Scheme 19.

In 2021, Sarvari and Valikhani reported high yielding synthesis of 2-phenyl-1-thiocyanatopropan-2-ol **29** *via* photocatalyzed hydroxy-thiocyanation of α-methylstyrenes **28** (a 1,1-disubstituted alkene) employing B-TiO_2 as the catalyst in MeCN at 0 °C (Scheme 20) [27]. Notably, when mono-substituted alkenes were subjected to these reaction conditions, the corresponding α-thiocyanatoketones were exclusively obtained without any of hydroxy-thiocyanated product (see section 2).



28, (1 mmol) **29**, (85%)

Scheme 20. Sarvari-Valikhani's synthesis of β-thiocyanato alcohols **27**.

5. Hydroxy-thiocyanation of alkynes

Unfortunately, a careful scan of literature revealed that there is still no reported guidance for the construction of β-thiocyanato alcohols through the direct hydroxy-thiocyanation of alkynes. We hope that this Mini-Review will stimulate researchers to conduct further research in this area so that the direct synthesis of β-thiocyanato alcohols from the respective alkynes become a reality.

6. Conclusion

The direct difunctionalization of unsaturated hydrocarbons, installation of two new functional groups across the double/triple bond of an alkene/alkyne, is a powerful method to create complex molecular structures from simple and readily available feedstocks. In this domain, thiocyanative difunctionalization of unsaturated hydrocarbons via three-component transformations is became a well-established method for the synthesis of functionalized organic thiocyanates. α-Thiocyanatoketones and β-thiocyanato alcohols are two important class of organic thiocyanates that are recognized as powerful and valuable building blocks for organic synthesis. Recently, the direct oxy-/hydroxy-thiocyanation of unsaturated hydrocarbons have become a valuable tool to achieve these family of organic thiocyanates withing a single click under benign conditions. In this review, we have summarized the current literature on direct oxy-/hydroxy-thiocyanation reactions with the hope of encouraging scientists to further research on this interesting research area.

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