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Metal-free difunctionalization of alkynes leading to alkenyl dithiocyanates and alkenyl diselenocyanates at room temperature†

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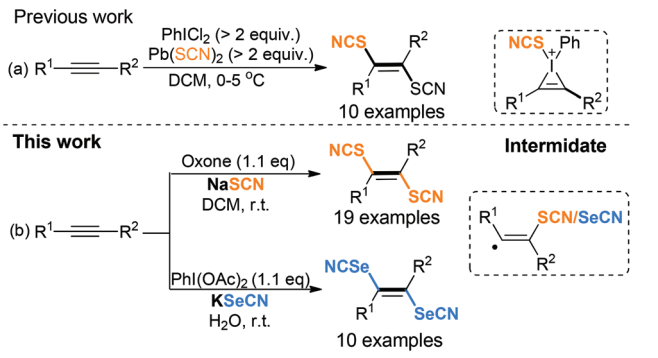
A simple and practical method for the synthesis of alkenyl dithiocyanates and alkenyl diselenocyanates has been developed *via* stereoselective difunctionalization of alkynes with NaSCN or KSeCN at room temperature. Through this methodology, a series of alkenyl dithiocyanates and alkenyl diselenocyanates could be efficiently and conveniently obtained in moderate to good yields under mild and metal-free conditions by the simple use of oxone and $PhI(OAc)_2$ as the oxidants.

Introduction

As a key structural motif, the thiocyanato group is widely present in a variety of natural products, biologically active compounds and synthetic intermediates.[1] Thus, the introduction of the thiocyanato group into organic molecules has drawn much attention from chemists in terms of their important biological properties[2] and widespread synthetic applications for the construction of diverse valuable sulfur-containing compounds such as disulfides,[3] thioethers,[4] thiocarbamates[5] and sulfonylcyanides.[6] Although many methods have been established to synthesize alkyl[7] and aryl thiocyanates,[8] the construction of alkenyl thiocyanates has not been fully developed, in spite of their versatile transformation abilities in organic synthesis. Generally, alkenyl thiocyanates are prepared through the nucleophilic substitution of vinyl halides with thiocyanate salts.[9] Other elegant methods for the synthesis of alkenyl thiocyanates have also been developed.[10] Among them, the functionalization of alkynes with [SCN] reagents represents one of the most powerful and straightforward methods for the construction of alkenyl thiocyanates due to their high atom economy and reaction efficiency. For example, Jiang and coworkers presented silver catalyzed hydrothiocyanation of haloalkynes with KSCN in AcOH at 100 °C leading to *Z*-alkenyl thiocyanates.[10c] In the same year, Yan and coworkers developed a facile and mild protocol to obtain allyl isothiocyanates through iodothiocyanation of allenes with KSCN and molecular iodine.[10d] In 2017, Sridhar Reddy *et al.* described the addition reaction of electron-deficient alkynes with KSCN in acetic acid for the synthesis of alkenyl thiocyanates.[10e] Very recently, our group also reported ultrasound-promoted Brønsted acid ionic liquid catalyzed hydrothiocyanation of activated alkynes with KSCN to access *Z*-alkenyl thiocyanates.[10f] However, all of these methods are limited to the hydrothiocyanation of alkynes leading to mono-alkenyl thiocyanates. To the best of our knowledge, only one example has been reported on the construction of alkenyl dithiocyanates from alkynes, (dichloroiodo)benzene and lead(II) thiocyanate through an iodirenium ion intermediate[11] (Scheme 1a). Obviously, the utilization of stoichiometric amounts of lead(II) reagent would increase the risk for traces of toxic metals in the products and limit their wide applications in the field of synthetic and pharmaceutical chemistry. Therefore, the development of a facile, efficient,



Scheme 1 Methods for the synthesis of alkenyl dithiocyanates and alkenyl diselenocyanates.

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practical and eco-friendly protocol for the construction of alkenyl dithiocyanates is still in high demand.

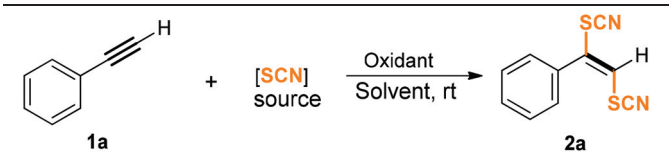
With our continued interest in green synthesis,[12] we have reported the eco-friendly functionalization of alkynes.[13] In this paper, we wish to report a facile, efficient and metal-free method for the construction of various alkenyl dithiocyanates *via* stereoselective difunctionalization of alkynes[14] with NaSCN at room temperature by simply using cheap oxone as the oxidant (Scheme 1b). In contrast to the known $PhICl_2$/Pd $(SCN)_2$ mediated dithiocyanation of alkynes, the present reaction proceeds through an alternative radical process. Moreover, this protocol could also be expanded to construct the corresponding alkenyl diselenocyanates through $PhI(AcO)_2$ mediated 1,2-diselenocayanation of alkynes with KSeCN in water (Scheme 1b).

Results and discussion

Initially, the reactions of phenylacetylene (**1a**) with [SCN] sources such as KSCN, NaSCN and NH_4SCN were investigated in the presence of $K_2S_2O_8$ (1.1 equiv.) in DCM at room temperature under air (Table 1, entries 1–3). Among these tested [SCN] sources, NaSCN was found to be the most effective one to produce the product **2a** in 76% yield (entry 2).[15] Next, various oxidants including $Na_2S_2O_8$, $(NH_4)_2S_2O_8$, *tert*-butyl hydroperoxide (TBHP), di-*tert*-butyl peroxide (DTBP), $PhI(OAc)_2$, oxone, H_2O_2, *tert*-butyl peroxybenzoate (TBPB), benzoyl peroxide (BPO), dicumyl peroxide (DCP), $PhICl_2$ and dioxygen were explored by using NaSCN as the [SCN] source (entries 4–15). Among various oxidants examined, oxone turned out to be the best choice in terms of high reaction efficiency and low-cost (entry 9). No thiocyanation reaction was observed when an acid promoter was used instead of Oxone (entries 16 and 17). Further optimization of solvents suggested that DCM was the best reaction medium. When the reaction was performed in DCE, PhCl or toluene, the desired product **2a** was also obtained in moderate to good yields (entries 18–20). In contrast, the reaction did not occur in CH_3CN, DMF, DMSO, H_2O, EtOAc, or THF (entries 21–26). The reaction efficiency was not obviously improved by increasing the amount of oxidant or reaction temperature (entries 27–29). In addition, treatment of **1a** with 1.1 equiv. of KSCN could not deliver any monothiocyanate product (entry 30). After an extensive screening of the reaction parameters, the best yield of product **2a** (80%) was obtained by employing NaSCN (2.2 equiv.) and oxone (1.1 equiv.) in DCM at room temperature.

Upon optimization of reaction conditions (Table 1, entry 9), the substrate scope for the 1,2-dithiocyanation of alkynes with KSCN was surveyed. As shown in Table 2, this difunctionalization reaction proceeded with excellent stereoselectivity and alkenyl dithiocyanates could be effectively obtained in moderate to good yields. A series of phenylacetylene derivatives bearing electron donating groups (Me and OMe) and electron withdrawing groups (F, Cl, and Br) produced the corres-

Table 1 Optimization of reaction conditions[a]

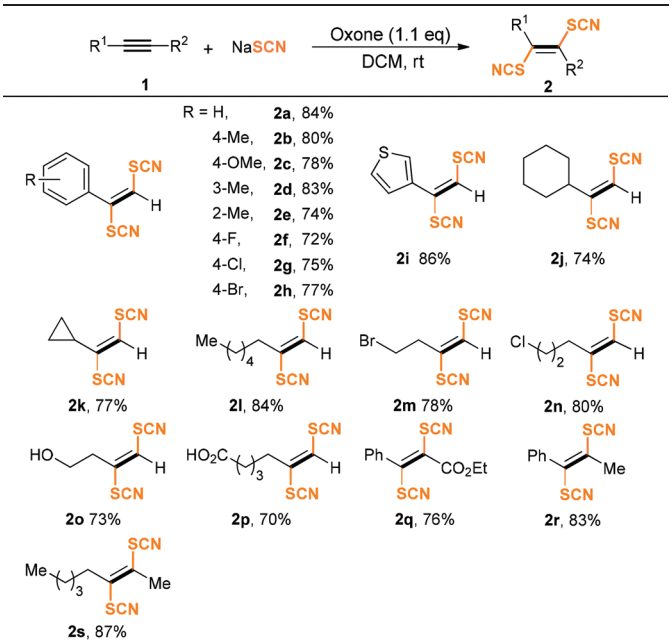


1a **2a**

Entry	[SCN] (X equiv.)	Oxidant (equiv.)	Solvent	Yield[b] (%)
1	KSCN (2.2)	$K_2S_2O_8$ (1.1)	DCM	31
2	NaSCN (2.2)	$K_2S_2O_8$ (1.1)	DCM	76
3	NH_4SCN (2.2)	$K_2S_2O_8$ (1.1)	DCM	22
4	NaSCN (2.2)	$Na_2S_2O_8$ (1.1)	DCM	Trace
5	NaSCN (2.2)	$(NH_4)_2S_2O_8$ (1.1)	DCM	26
6	NaSCN (2.2)	TBHP (1.1)	DCM	ND
7	NaSCN (2.2)	DTBP (1.1)	DCM	ND
8	NaSCN (2.2)	$PhI(OAc)_2$ (1.1)	DCM	33
9	**NaSCN (2.2)**	**Oxone (1.1)**	**DCM**	**80**
10	NaSCN (2.2)	H_2O_2 (1.1)	DCM	ND
11	NaSCN (2.2)	TBPB (1.1)	DCM	ND
12	NaSCN (2.2)	BPO (1.1)	DCM	ND
13	NaSCN (2.2)	DCP (1.1)	DCM	ND
14	NaSCN (2.2)	$PhICl_2$ (1.1)	DCM	31
15	NaSCN (2.2)	O_2 balloon	DCM	ND
16	NaSCN (2.2)	HOAc (1.1)	DCM	ND
17	NaSCN (2.2)	BAIL (1.1)	DCM	ND
18	NaSCN (2.2)	Oxone (1.1)	DCE	32
19	NaSCN (2.2)	Oxone (1.1)	PhCl	54
20	NaSCN (2.2)	Oxone (1.1)	Toluene	71
21	NaSCN (2.2)	Oxone (1.1)	CH_3CN	ND
22	NaSCN (2.2)	Oxone (1.1)	DMF	ND
23	NaSCN (2.2)	Oxone (1.1)	DMSO	ND

[a] Conditions: **1a** (0.2 mmol), [SCN] source, oxidant, solvent (1 mL), air, rt, 2 h. [b] Isolated yields based on **1a**. BAIL: 1-(3 sulfopropyl)pyridin-1-ium hydrosulfate.

Table 2 Scope of alkenyl dithiocyanates[a,b]



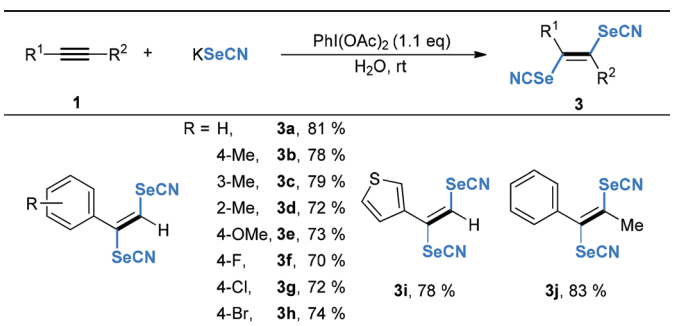
[a] Reaction conditions: **1** (0.2 mmol), NaSCN (0.44 mmol), oxone (0.22 mmol), DCM (1 mL), rt, 2 h. [b] Isolated yields based on **1**.

ponding products in good yields (**2b–2h**). However, when 1-ethynyl-4-(trifluoromethyl)benzene was used as the substrate, only a trace amount of the dithiocyanation product was observed. Heterocycle alkynes such as 3-ethynylthiophene would participate in the reaction to give the corresponding product **2i** in 86% yield. Only a trace amount of (*E*)-3-(1,2-dithiocyanatovinyl)pyridine was observed when 3-ethynylpyridine was subjected under the standard conditions. Various alkyl alkynes with hexatomic and triatomic rings as well as with long aliphatic chains were also effectively reacted with NaSCN to achieve products (**2j–2p**) in good yields. Notably, a series of functional groups such –Br, –Cl, –OH, and $–CO_2H$ groups could well be compatible with the reactions, thereby facilitating possible further modifications. Moreover, the corresponding alkenyl dithiocyanates (**2q–2s**) could also be produced in good yields when internal aromatic and aliphatic alkynes were used in the present reaction system.

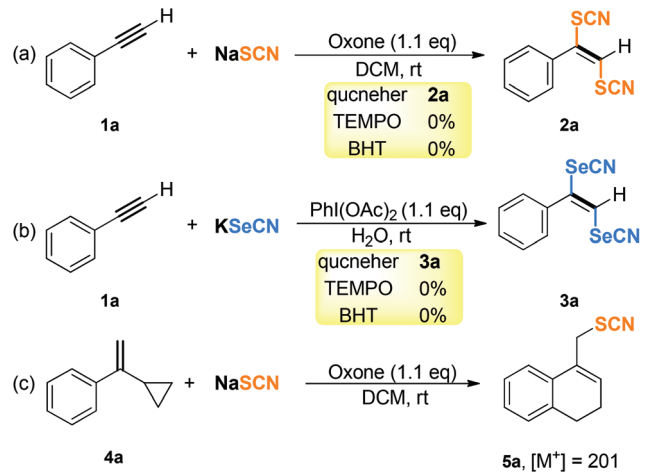
Organic selenocyanates are also versatile building blocks for the construction of structurally diverse seleno-containing compounds known to possess potent biological activities.[16] Subsequently, we turned our attention to explore the reaction of 1,2-diselenocyanation of alkynes. After an extensive screening of the reaction parameters for the model reaction between 4-methylphenylacetylene **1a** and KSeCN (see ESI, Table S1†), the highest yield (81%) of the desired alkenyl diselenocyanate **3a** was obtained when the reaction was carried out using $PhI(OAc)_2$ (1.1 equiv.) as the oxidant in H_2O at room temperature. Upon optimization of reaction conditions, the substrate scope for this transformation was surveyed. As shown in Table 3, the reaction could proceed well by using diverse aromatic alkynes with an electron-donating group or an electron-withdrawing group on the aromatic ring so as to form the corresponding products in moderate to good yields. Heterocyclic alkynes such as 3-ethynylthiophene and internal alkynes such as prop-1-ynylbenzene were also suitable for this reaction, with the desired products **3i** and **3j** obtained in 78% and 83% yields, respectively.

It is known that SCN radicals can be easily generated from the [SCN] source such NaSCN and KSCN in the presence of an oxidant,[17] which indicates that the present transformation

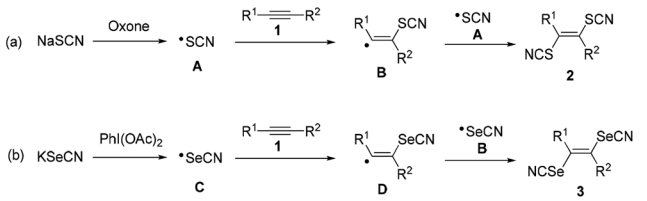
Table 3 Scope of alkenyl diselenocyanates[a,b]



[a] Reaction conditions: **1** (0.2 mmol), KSeCN (0.44 mmol), oxone (0.22 mmol), DCM (1 mL), rt, 2 h. [b] Isolated yields based on **1**.



Scheme 2 Control experiments.



Scheme 3 Proposed mechanism.

might also proceed through a radical process. As shown in Schemes 2a and b, when TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and BHT (2,6-di-*tert*-butyl-4-methylphenol), well-known radical-capturing species, were added into the reaction system under the standard conditions, this reaction was significantly inhibited. When (1-cyclopropylvinyl)benzene (**4a**) was used as a radical-clock substrate, the ring-opened product (**5a**) was obtained (Scheme 2c). The above results suggested that the present difunctionalization of alkynes might involve a radical process.

Based on the above results and previous reports,[17,18] a possible reaction pathway of the radical difunctionalization of alkynes is proposed in Scheme 3. Initially, the SCN radical[17] **A** or the SeCN radical **C** was generated from NaSCN or KSeCN in the presence of an oxidant. Subsequently, the anti-Markovnikov addition of the SCN radical **A** or the SeCN radical **C** to alkyne **1** produced the alkenyl radical **B** or **D**. Finally, the SCN radical **A** or the SeCN radical **C** attacked more favorably the sterically less hindered side of the alkenyl radical **B** or **D** which would lead to the formation of desired products **2** and **3**, respectively.

Conclusions

In conclusion, we have successfully developed a facile and practical method for the synthesis of various alkenyl dithiocyanates and alkenyl diselenocyanates *via* stereoselective

1,2-dithio/selenocyanation of alkynes with inexpensive NaSCN/KSeCN at room temperature. The present reaction features a relatively broad substrate scope, excellent functional group compatibilities, mild conditions, and cheap and less-toxic oxidants, and offers various alkenyl dithiocyanates and alkenyl diselenocyanates in moderate to good yields. Preliminary mechanistic studies revealed that the reaction might involve a radical process. Further studies of the detailed reaction mechanism and the synthetic applications are currently ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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