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$K_2S_2O_8$-mediated regio- and stereo-selective thiocyanation of enamides with NH_4SCN†

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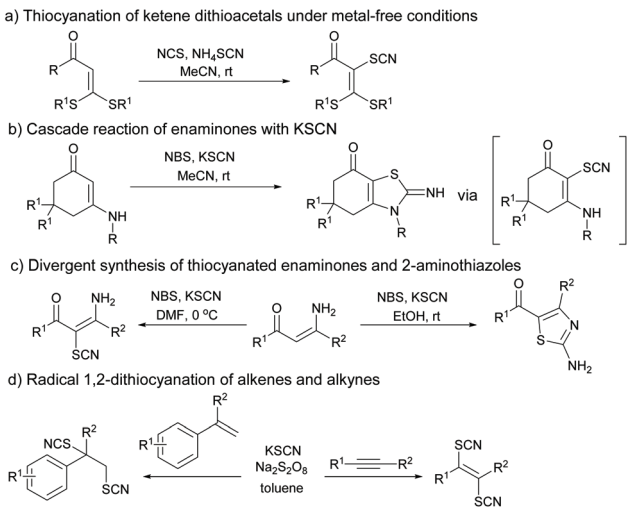
A direct and straightforward thiocyanation of enamides with NH_4SCN under metal-free conditions has been accomplished. A variety of (*E*)-β-thiocyanoenamides are readily produced in a regio- and stereo-selective manner. The protocol features mild reaction conditions, good functional group tolerance and operational simplicity. The potential utility of this strategy was further demonstrated by transformation of thiocyanate into thiotetrazole-containing compounds and a Pd-catalyzed cross-coupling reaction to afford six- or seven-membered sulfur-containing heterocycles. Mechanistic insights into the reaction indicate that the reaction may proceed *via* a radical mechanism.

Introduction

Enamides are attractive and versatile building blocks in modern synthetic chemistry since they can be readily converted to a wide range of pharmaceutically and biologically important molecules[1] and chiral amines.[2] Thus, the direct β-C(sp^2)–H functionalization of enamides including arylation,[3] alkynylation,[4] olefination,[5] acylation,[6] alkylation,[7] phosphorylation,[8] sulfonylation,[9] and others[10] has been achieved *via* transition-metal catalysis or radical coupling reactions in the past few decades. Despite the great progress achieved, the direct regio- and stereo-selective construction of β-thiocyanoenamides has remained unexplored.

On the other hand, organic thiocyanates are versatile precursors, which can be easily transformed into valuable sulfur-containing compounds such as thioethers, sulfides and sulfur-containing heterocycles,[11] and they are also prevalent in the field of biomedical and organic chemistry.[12] In this scenario, much effort has been devoted to the development of more simple and safe methods to access organic thiocyanates.[13] Although diverse strategies towards thiocyanation of aromatics[14] and heterocycles[15] have been developed, approaches for the direct thiocyanation of alkenes are less studied.[16]

In 2017, Wang and coworkers innovatively reported the thiocyanation of ketene dithioacetals in the presence of NCS and NH_4SCN under transition-metal free conditions, leading to thiocyanated alkene derivatives in excellent yields (Scheme 1a).[16a] In the same year, Liu and coworkers demonstrated an efficient construction of 2-iminothiazoles *via* the cascade reaction of cyclic enaminones with KSCN (Scheme 1b).[16b] Recently, the strategy was further applied to the solvent-dependent divergent synthesis of thiocyanated enaminones and 2-aminothiazoles by Duan and coworkers (Scheme 1c).[16c] It should be noted that these protocols in the presence of NXS/SCN^- (X = Cl or Br) all proceeded through the nucleophilic substitution reaction mechanism of tri-substituted alkenes with thiocyanating reagents; additionally, the generality of these protocols was investigated only with elec-



Scheme 1 Thiocyanation of alkenes or alkynes.

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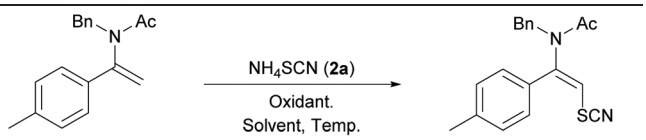
tron-withdrawing carbonyl group substituted alkenes. It is worth mentioning that Majee and co-workers elegantly extended the substrate scope to unactivated alkenes and alkynes in the presence of persulfate and thiocyanating reagents *via* a radical reaction mechanism to obtain various 1,2-dithiocyanated compounds under mild conditions in a short reaction time (Scheme 1d).[16e]

Considering the importance of organic thiocyanates, the exploration of an alternative method to construct such a desirable framework in a regio- and stereo-selective manner is still attractive. As part of our ongoing studies on the development of radical involving reactions,[17] we report herein a direct and straightforward thiocyanation of enamides with NH_4SCN under mild reaction conditions to regio- and stereo-selectively provide a diverse array of β-thiocyanoenamides in moderate to good yields.

Results and discussion

We commenced our investigation by choosing **1a** as the model substrate, NH_4SCN (**2a**) as the thiocyanate source, and NBS as an oxidant in CH_3CN at r.t.; it was found that **3aa** was obtained in 31% yield and **1a** was recovered in 63% yield (Table 1, entry 1). Then we examined several oxidants. To our delight, when $K_2S_2O_8$ was used as the oxidant, the yield increased to 76% (entry 2); $Na_2S_2O_8$ was more efficient than TBHP to afford **3aa** in 72% yield (entries 3 and 4), and the reaction could not be carried out without an oxidant (entry 5). Among the solvents tested, AcOH was found to be superior to other solvents such as THF or toluene, and the yield of **3aa** was increased to 81% (entries 6–8).

Table 1 Optimization of reaction conditions[a]



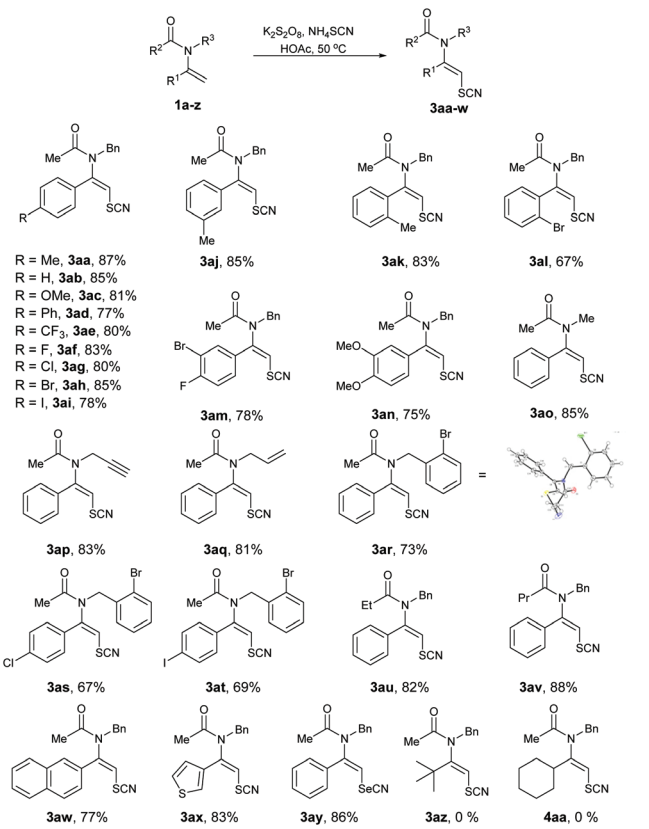
1a 3aa

Entry	Oxidant	Solvent	Temp. (°C)	Yield[b] (%)
1	NBS	CH_3CN	r.t.	31
2	$K_2S_2O_8$	CH_3CN	r.t.	76
3	$Na_2S_2O_8$	CH_3CN	r.t.	72
4	aq. TBHP	CH_3CN	r.t.	45
5	—	CH_3CN	r.t.	n.r.
6	$K_2S_2O_8$	AcOH	r.t.	81
7	$K_2S_2O_8$	THF	r.t.	35
8	$K_2S_2O_8$	Toluene	r.t.	65
9	$K_2S_2O_8$	AcOH	50	87
10	$K_2S_2O_8$	AcOH	80	86
11[c]	$K_2S_2O_8$	AcOH	50	85
12[d]	$K_2S_2O_8$	AcOH	50	80

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), oxidant (0.45 mmol), solvent (2 mL) at the indicated temperature for 6 h. [b] Isolated yield. [c] **1a : 2a** = 1 : 2. [d] **1a : 2a** = 1 : 1.

After screening various reaction conditions, including oxidants and solvents, we gratifyingly obtained the desired thiocyanated product **3aa** in 87% yield by increasing the temperature to 50 °C (entry 9), while continuously increasing the temperature to 80 °C resulted in a similar yield (entry 10). Finally, by fine tuning the ratio of **1a : 2a** (entries 11 and 12), the optimal reaction conditions were determined as shown in entry 9.

With the optimal conditions established, we set out to investigate the generality of this reaction, and the results are summarized in Scheme 2. The protocol is applicable to a wide range of enamides to afford the desired products **3aa-y** in moderate to good yields. The reaction is not affected by the electronic properties of the substituents; enamides bearing electron-donating groups (–Me, –OMe, –Ph) or electron-withdrawing groups (–CF_3, F, Cl, Br, I) at the *para*-position were tolerated to afford **3aa-i** in good yields. Notably, the halide substituents are compatible in the reaction to give **3ag-i** and **3al** in 67–85% yields, which are amenable for further elaboration. The reaction efficiency is not affected by the steric hindrance of the substituents, to afford **3aj** and **3ak** in comparable yields to **3aa**. Apart from enamides with a mono-substituent at the phenyl ring, enamides with di-substituents at the phenyl ring are also suitable substrates in the reaction to deliver the corresponding products in good yields (**3am**, **3an**).



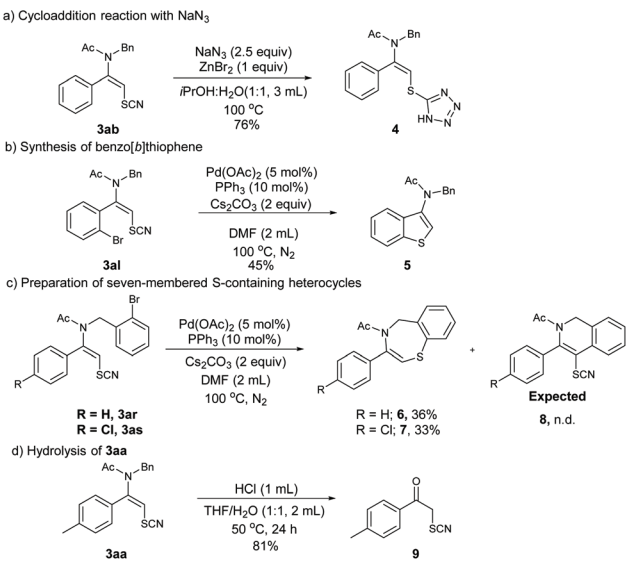
Scheme 2 Substrate scope of radical thiocyanation of enamides. Reactions were carried out with enamides (**1a-z**) (0.3 mmol), NH_4SCN (1.5 equiv.) and $K_2S_2O_8$ (1.5 equiv.) in HOAc (2 mL) at 50 °C for 6 h.

With the results obtained above, the substituents tethering to the nitrogen atom are also examined. Changing benzyl-protected enamides to alkyl-, allyl- or propargyl-protected enamides afforded the target products in comparable yields (**3ao-q**). Notably, excellent regio-selectivity is observed in our reaction to furnish **3ap** and **3aq** as mono-thiocyanated products even with an increasing amount of NH_4SCN and a prolonged reaction time. In addition, substituents on the phenyl ring of the benzyl group are also compatible to afford **3ar-t** in acceptable yields. The structure of **3ar** was unambiguously confirmed by X-ray single crystal diffraction (CCDC 2014798†). When replacing the –Me group with –Et and –Pr, **3au** and **3av** are obtained in good yields. Additionally, naphthyl- and thienyl-substituted enamides also participate in the reaction to deliver **3aw** and **3ax** in 77% and 83% yield, respectively. To our delight, **3ay** is formed in 86% yield using KSeCN as the selenium source. Unfortunately, when aliphatic enamides were subjected to the standard conditions, no reaction occurred (**3az**, **4aa**). Based on the X-ray structure determination for compound **3ar**, the stereochemistry of the other compounds in Scheme 2 is tentatively assigned as *E*. The excellent stereo-selectivity is likely attributed to the steric repulsion between the SCN group and protected amide group.

To further expand the application of this protocol, thiotetrazole **4** was prepared in 76% yield *via* the cycloaddition reaction of **3ab** with NaN_3 (Scheme 3a). Next, a Pd-catalyzed intramolecular cross-coupling cyclization reaction was successfully conducted to obtain benzo[*b*]thiophene **5** in 45% yield (Scheme 3b). Notably, we are surprised to find that the expected product **8** was not detected in the Pd-catalyzed cross-coupling reaction of **3ar** and **3as**, instead, the seven-membered rings **6** and **7** were obtained in 36% and 33% yield, respectively, probably through the initial isomerization of **3ar** and **3as**, followed by the Pd-catalyzed C–S bond formation reaction (see the ESI† for details about the plausible mechanism), which was in stark contrast to the previous report where the six-membered ring as a single product was obtained through the Heck reaction (Scheme 3c).[1g,6g,7f,h] Furthermore, the hydrolysis of **3aa** was easily achieved to obtain α-thiocyanoketone **9** in good yield, which is a versatile synthon that could be transformed to various sulfur-containing bioactive scaffolds (Scheme 3d).[18]

To probe the mechanism of the developed protocol, control experiments were performed in the presence of a radical scavenger (Scheme 4). It was found that the corresponding product **3ab** was obtained in trace or 23% yield upon the addition of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Scheme 4a); the results showed that a radical process may be involved in this reaction. The radical intermediate could further be trapped by 1,1-diphenylethylene (DPE) to afford the adduct of DPE and SCN radical **10** in 31% yield (Scheme 4b).

Based on the results obtained above and previous reports,[3–10] a plausible reaction mechanism was proposed as shown in Scheme 5; initially, the reaction of NH_4SCN with $K_2S_2O_8$ could generate a SCN radical ($^{\bullet}$SCN); the *in situ* generated SCN radical undergoes an addition process with enamides (**1b**) to afford intermediate **A**, which was further oxidized to yield a cationic intermediate **B**. We believe that intermediate **B** could possibly go through either path I or path II to afford **3ab** as *E* isomer. As depicted in path I, product **3ab** could be formed through the deprotonation of intermediate **B**. The stereo-selectivity could be attributed to the steric repulsion between the protected amide group and the SCN group, resulting in the sterically more favourable *E*-type products. While a more convincible pathway was also proposed as path II, carbon cationic species **B** would resonate to iminium ion **C**, which could undergo [1,5]-σ rearrangement to furnish intermediate **D**, followed by loss of the proton to give **3ab** as an *E* isomer.

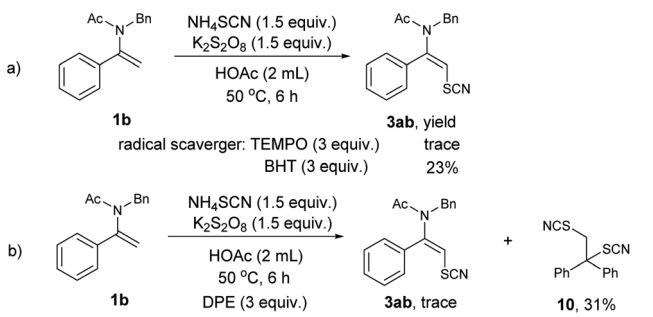


Scheme 3 Synthetic applications.

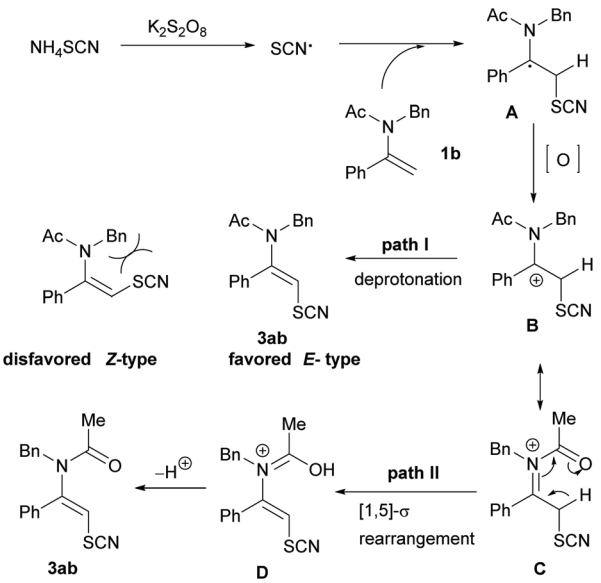
Experimental section

General procedure for the syntheses of 3aa-y

A mixture of enamides (**1a-y**) (0.3 mmol), NH_4SCN (34.2 mg, 0.45 mmol, 1.5 equiv.) and $K_2S_2O_8$ (121.5 mg, 0.45 mmol, 1.5 equiv.) in HOAc (2 mL) was stirred at 50 °C for 6 h (monitored



Scheme 4 Preliminary mechanistic studies.



Scheme 5 Plausible mechanism.

by TLC). After it was cooled down to room temperature, the reaction was quenched by the slow addition of a saturated solution of Na_2CO_3. The mixture was poured into water (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (2 × 15 mL) and dried over $MgSO_4$. The solvent was removed by vacuum and the residue was purified by column chromatography (10% EtOAc in PE) to give the corresponding products **3aa-y**.

Conclusions

In conclusion, we have developed a robust and efficient method for the radical thiocyanation of enamides with NH_4SCN to afford a variety of (*E*)-β-thiocyanoenamides in a regio- and stereo-selective manner. The synthetic practicability of this method was shown by transforming thiocyano-enamides into important sulfur-containing scaffolds. Control experiments indicated that the reaction proceeded through a radical mechanism. Therefore, we expected this protocol to serve as an attractive tool to access a variety of sulfur-containing heterocycles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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