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N-heterocyclic carbene-catalyzed regio- and stereoselective hydrothiolation reaction of alkynes

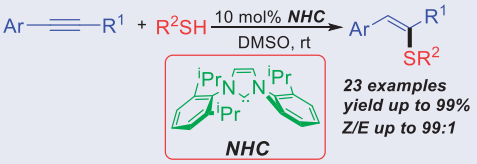
Zi-Song Cong, Yang Zhang, Guang-Fen Du, Cheng-Zhi Gu, and Lin He

Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Xinjiang Uygur, Autonomous Region, People's Republic of China

ABSTRACT

N-heterocyclic carbenes (NHCs) have been utilized as Brønsted base to catalyze the hydrothiolation reaction between alkynes and thiols to produce the vinyl sulfides stereoselectively.

GRAPHICAL ABSTRACT



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KEYWORDS
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N-heterocyclic carbene;
vinyl sulfide

Introduction

Vinyl sulfides are significant structural motifs found in natural products, biologically active compounds and functional materials.[1] The most atom-economical and straightforward method to synthesize vinyl sulfides is hydrothiolation reaction of alkynes.[2] Over the past several decades, many different transition metal catalysts[3] have been explored for the synthesis of vinyl sulfides. However, some of those methods suffer some drawbacks like the use of expensive transition metals or low *Z*/*E* selectivity. Base-mediated addition of thiols to alkynes was developed firstly by Truce[4] and co-workers, more than half century ago, but the stoichiometric amount of a base was necessary. Recently, Oshima and co-workers reported[5] that catalytic amount of cesium carbonate can promote this hydrothiolation reaction efficiently. However, the radical inhibitor TEMPO was needed and aryl thiols were unsuccessful for the addition. Despite great progress made in this research, the development of more efficient and mild protocols for the syntheses of vinyl sulfides is still of high importance.

CONTACT Guang-Fen Du duguangfen@shzu.edu.cn Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Xinjiang Uygur Autonomous Region 832000, People's Republic of China.

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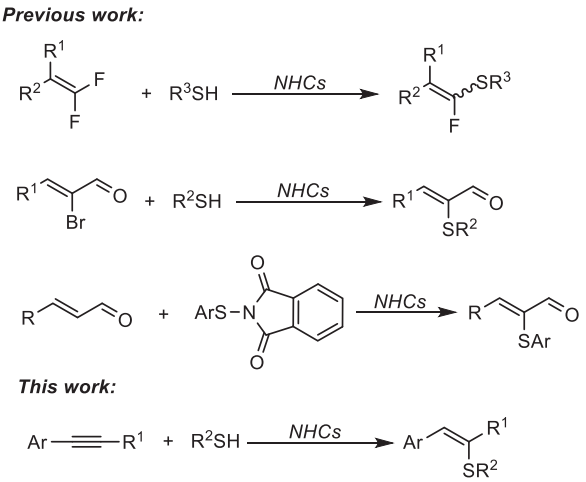
Supplemental material (^{1}H and ^{13}C NMR spectra and experimental details) can be accessed on the publisher's website.

As an important type of organic catalysts, NHCs have been utilized widely in different transformations.[6] In addition to the classical benzoin condensation[7] and Stetter reaction,[8] NHCs-catalyzed homoenolate transformation,[9] redox reaction,[10] cycloaddition,[11] and other reactions[12] have been extensively studied in the past decades. Those aforementioned reactions are mainly based on the Lewis basic properties of NHCs. On the other hand, NHCs have unique Brønsted base characteristics. Nolan and Hedrick independently developed NHC-catalyzed transesterifications.[13] The mechanism study revealed that NHC acted as a Brønsted base to promote the transformation.[14] Using the specific Brønsted base properties, NHCs-catalyzed Michael type additions between different nucleophiles and Michael acceptors have been developed by Conquerel,[15] Scheidt,[16] Zhang,[17] Huang,[18] and our group.[19] Very recently, we[20a,b] found that NHCs can catalyze the reactions of thiols and active alkenes to form functionalized vinyl sulfides. Zhou, Chen, and co-workers[20c] also reported an interesting method to synthesize this motifs via NHC-catalyzed sulfenylation reaction of α,β-unsaturated aldehydes. Based on these works, we envisioned that NHCs can function as a Brønsted base to catalyze the hydrothiolation reaction of alkynes (Scheme 1). And herein, we wish to report this result.

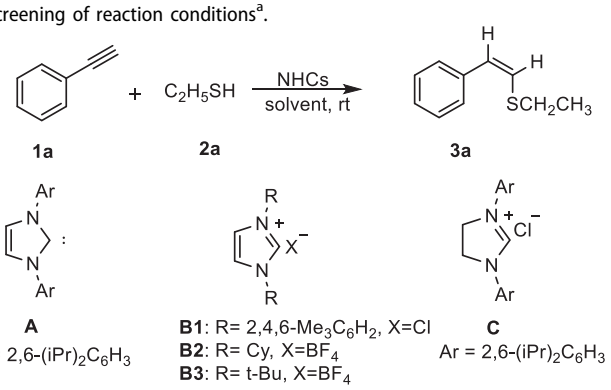
Experimental

Our initial studies were carried out with the commercially available phenylacetylene **1a** and ethanethiol **2a** as the model substrates (Table 1). Treatment of **1a** with 1.5 equiv **2a** in the presence of the 10 mol% stable N-heterocyclic carbene **A**[21] in THF at room temperature for 10 h afforded the adduct **3a** in 57% yield with moderate *Z/E* selectivity. The following studies showed that the reaction media has dramatic influence on the reaction yield and *Z/E* selectivity. Only trace amount of the hydrothiolation adduct was obtained in low polarity solvents (Table 1, entries 2–4). Conversely, high yield and *Z/E* selectivity were obtained in high polarity solvents (Table 1, entries 5–7). Under similar conditions, other NHCs derived from imidazolium salts can catalyze the addition efficiently to give **3a** in good yield with high *Z/E* selectivity (Table 1, entries 8–10). NHC generated from the saturated imidazolinium **C** showed relatively low activity, affording the product in



Scheme 1. NHCs-catalyzed synthesis of vinylsulfides.

Table 1. Screening of reaction conditions[a].



Entry	Conditions	Time (h)	Yield (%)[b]	*Z/E*[c]
1	**A** (10 mol%), THF	10	57	5:3
2	**A** (10 mol%), DCM	10	trace	/
3	**A** (10 mol%), toluene	10	trace	/
4	**A** (10 mol%), DCE	10	trace	/
5	**A** (10 mol%), CH_3CN	10	73	17:1
6	**A** (10 mol%), DMSO	10	87	17:1
7	**A** (10 mol%), DMF	10	66	17:1
8	$\mathbf{B_1}$, Cs_2CO_3(10 mol%), DMSO	10	64	14:1
9	$\mathbf{B_2}$, Cs_2CO_3(10 mol%), DMSO	10	70	17:1
10	$\mathbf{B_3}$, Cs_2CO_3(10 mol%), DMSO	10	71	11:1
11	**C**, Cs_2CO_3(10 mol%), DMSO	10	44	14:1
12	**A** (5 mol%), DMSO	24	50	17:1

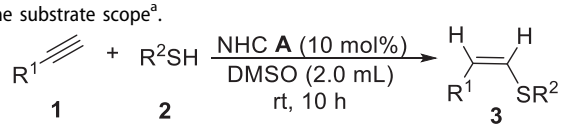
[a]**1a** (1 equiv., 0.2 mmol), **2a** (2.0 equiv., 0.4 mmol), NHCs (10 mol%), solvent (2.0 mL).
[b]Isolated total yield of *Z/E* stereoisomers.
[c]*Z/E* was determined by ^{1}H NMR analysis of the crude products.

moderate yield with high *Z/E* selectivity (Table 1, entry 11). Reduction NHC loading to 5 mol% led to a dramatic decrease of the reaction yield (Table 1, entry 12).

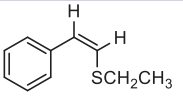
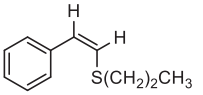
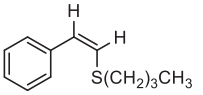
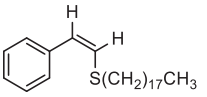
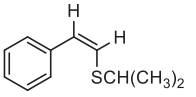
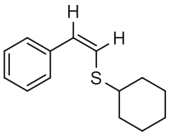
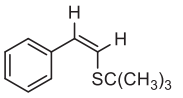
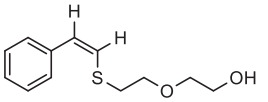
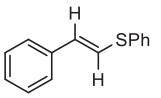
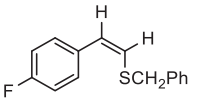
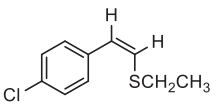
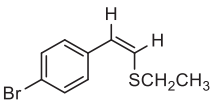
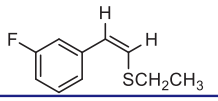
Results and discussion

With the optimal conditions in hand (Table 1, entry 6), we examined the scope and generality of the reaction. As shown in Table 2, primary, secondary, and the sterically hindered tertiary thiols can react with phenyl acetylene **1a** to produce the desired products in good to excellent yields with high *Z/E* selectivities (Table 2, entries 1–7). More interestingly, the free hydroxy group of 2-(2-mercaptoethoxy)ethanol can be tolerated for the reaction, producing **3h** in 90% yield with >99:1 *Z/E* selectivity (Table 2, entry 8). Intriguingly, thiophenol, which was proved to be unsuccessful in cesium carbonate-catalyzed hydrothiolation reaction,[5] reacted with phenyl acetylene smoothly to deliver **3i** in 52% yield, but with opposite stereoselectivities (Table 2, entry 9). We concluded that NHC can react with the acidic sulfhydryl group of thiophenol to form the free thioxy anion species, which further reacted with phenyl acetylene to give the desired product with *E*-selectivity. The scope of alkynes was next examined for the reaction. Electron-withdrawing groups substituted terminal alkynes reacted with thiols smoothly, producing the desired adducts in high yield and *Z/E* selectivity (Table 2, entries 10–12). Moreover, different positions of the substituents can be well tolerated for the reaction

Table 2. Evaluation of the substrate scope[a].

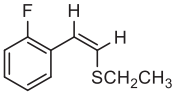
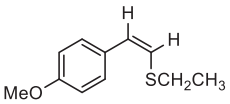
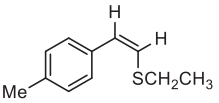
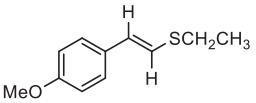
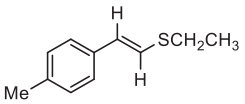
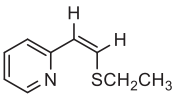
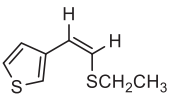
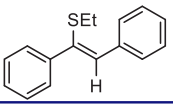


1 2 3

Entry	Product	Yield (%)[b]	*Z*/*E*[c]
1		**3a**, 87%	17:1
2		**3b**, 86%	17:1
3		**3c**, 83%	14:1
4		**3d**, 70%	6:1
5		**3e**, 88%	17:1
6		**3f**, 95%	20:1
7		**3g**, 92%	28:1
8		**3h**, 90%	>99:1
9		**3i**, 52%	1:4
10		**3j**, 88%	32:1
11		**3k**, 93%	10:1
12		**3l**, 89%	8:1
13		**3m**, 93%	6:1

(*continued*)

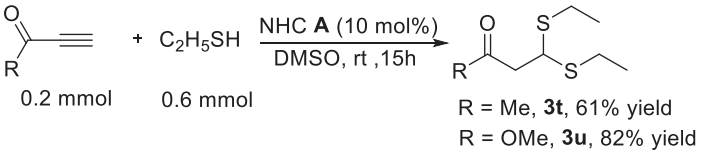
Table 2. Continued

Entry	Product	Yield (%)[b]	*Z*/*E*[c]
14		**3n,** 99%	13:1
15[d]		***Z*-3o,** 74%	1.3:1
16[d]		***Z*-3p,** 67%	2.5:1
17[e]		***E*-3o,** 93%	1:1.8
18[e]		***E*-3p,** 85%	1:2.5
19		**3q,** 99%	8:1
20		**3r,** 98%	50:1
21[d]		**3s,** 68%	17:1

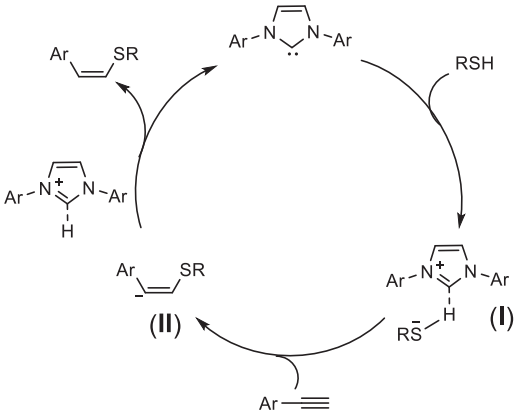
[a]**1** (0.2 mmol), **2** (0.3 mmol), NHC **A** (10 mol%), DMSO (2.0 mL), rt 10 h.
[b]Isolated total yield of *Z*/*E* isomers.
[c]*Z*/*E* was determined by ^{1}H NMR analysis of the crude products.
[d]**1** (0.2 mmol), **2** (0.6 mmol), rt 24 h.
[e]Conducted the reaction at 80 °C.

(Table 2, entries 13 and 14). However, when electron-donating groups substituted alkynes were used for the reaction, the hydrothiolation products can be formed in good yields but with dramatically decreased *Z*/*E* selectivity (Table 2, entries 15 and 16). More interestingly, when the reactions were conducted at 80 °C, *E*-vinyl sulfides were obtained as the main isomer (Table 2, entries 17 and 18). We concluded that the electron-donating substituents lowered the electrophilicity of alkynes and lead to the increase in the amount of the thermodynamic stable *E*-isomer. Notably, heteroaryl substituted alkynes were proven to be competent substrates, producing the corresponding products **3q** and **3r** in excellent yields and high *Z*/*E* selectivities, respectively (Table 2, entries 19 and 20). Diphenylacetylene is a very good candidate for the addition, furnishing **3s** in 68% yield with high *Z*/*E* ratio (Table 2, entry 21).

When the more active methyl ethynyl ketone and methyl propiolate were also tested for the reaction, the double sulfa-Michael products **3t** and **3u** were obtained in good yields (Scheme 2).



Scheme 2. Double hydrothiolation reaction.



Scheme 3. Proposed mechanism.

Based on the pioneering work on NHC-catalyzed transesterification and C–S bond forming reactions,[13,20] a plausible mechanism was proposed as depicted in Scheme 3. NHC functions as a Brønsted base to interact with a thiol to form NHC-thioxy species **I**, which undergoes nucleophilic addition with the triple bond of alkyne to form anion **II**, and after protonation to produce the final product with releasing of free NHC.

Conclusions

An organocatalytic hydrothiolation reaction of alkynes has been described. The mild and transition metal free conditions, simple procedure and generally high yield and *Z/E* selectivity provide a new protocol for the synthesis of vinyl sulfide products.

Experimental

General section

All reactions were conducted under the nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$), and ^{19}F NMR (376 MHz, $CDCl_3$) spectra were recorded using deuterated chloroform as a solvent, with tetramethylsilane as an internal standard and reported in ppm (δ). Melting points were measured on a WRS-1B melting point apparatus and were uncorrected. Thiols and other chemicals were obtained from Adamas-beta and used without purification. Anhydrous THF and toluene were distilled from sodium and

benzophenone. DMF, CH_2Cl_2, and CH_3CN were distilled from calcium hydride. DMSO was distilled from calcium hydride under vacuum. 1, 2-Dichloroethane was distilled from calcium chloride.

Typical procedure for NHC-catalyzed hydrothiolation reaction of alkyne

NHC **A** (7.8 mg, 10 mol%) was dissolved in 2.0 mL dry DMSO, followed by the addition of alkyne **1a** (20.4 mg, 0.2 mmol), and thiol **2a** (18.6 mg, 0.3 mmol) at ambient temperature. The reaction mixture was stirred at the same temperature for 10 h. Then, the mixture was diluted with EtOAc (30 mL), washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography on silica gel (PE) to give the desired product **3a**[22] as a colorless oil in 87% yield (28.5 mg); an inseparable 17:1 *Z/E* mixture; Data for *Z*-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.450–7.45 (m, 2H), 7.37-7.32 (m, 2H), 7.26–7.15 (m, 1H), 6.45 (d, $J = 10.9$ Hz, 1H), 6.25 (d, $J = 10.9$ Hz, 1H), 2.80 (q, $J = 7.4$ Hz, 2H), 1.35 (t, $J = 7.4$ Hz, 3H). Selected data for *E*-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, $J = 15.6$ Hz, 1H), 6.47 (d, $J = 16.2$ Hz, 1H). Data for *Z*-**3a**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 128.6, 128.2, 127.2, 126.6, 125.5, 29.7, 15.4.

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