Hydrothiolation of Alkenes and Alkynes Catalyzed by 3,4-Dimethyl-5-vinylthiazolium iodide and Poly(3,4-dimethyl-5-vinylthiazolium) iodide

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The highly selective anti-Markovnikov addition of thiols to unactivated alkenes and alkynes was demonstrated by using 3,4dimethyl-5-vinylthiazolium iodide or its polymer, poly(3,4-dimethyl-5-vinylthiazolium) iodide, as a complementary catalyst. The reaction proceeded cleanly under base-free conditions in air with both aromatic and aliphatic thiols. The polymer catalyst showed a high turnover number (\approx 5800) and could be reused up to four times without any loss of catalytic activity. DFT calculations supported stabilization of the thiyl radical intermediate by the thiazolium cation, which resulted in reaction of the radical with unsaturated C–C bonds.

Organosulfur compounds have widespread applications in materials chemistry and chemical biology.^[1] Thus, the development of efficient synthetic methods for the incorporation of sulfur into organic frameworks is of significant interest.^[2] In this context, the hydrothiolation reaction, that is, the direct addition of the S-H bond of thiols to unsaturated carbon-carbon bonds, is a simple and atom-economical approach to the synthesis of organosulfur compounds.^[3] The development of efficient catalytic systems that can promote hydrothiolation is an important challenge for synthetic organic chemists. Hydrothiolation can be catalyzed by strong bases,[4a-d] strong acids, or free radicals.^[4e, f] Recently, several metal compounds were revealed to catalyze hydrothiolation reactions and were reviewed.^[5] However, some of the reported procedures have many disadvantages, such as unsatisfactory yields, long reaction times,^[6] formation of unwanted byproducts, the use of highly carcinogenic and hazardous organic solvents,^[7] and the use of expensive and/or difficult to obtain catalysts.^[8] Thus, the development of a more efficient and convenient method for the hydrothiolation of alkenes and alkynes is necessary.

Organocatalysts are usually inexpensive, readily available, robust, and nontoxic.^[9] However, they are not usually reusable because of the difficulties involved in their recovery. To overcome the problems related to the isolation of these catalysts from a reaction mixture, we recently developed a polymerbased organocatalytic system, poly(4-vinyl N-heterocyclic carbene).^[10] Theses catalysts showed high activity in the cycload-

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Supporting Information for this article can be found under http:// dx.doi.org/10.1002/cctc.201600363. dition of CO₂ to epoxides, the benzoin condensation reaction, and the tandem formation of γ -butyrolactone from benzaldehyde and methyl acrylate. These polymer-based systems can be reused several times without any significant loss of catalytic activity. We also reported the synthesis of poly(3,4-dimethyl-5vinylthiazolium) iodide (**B**) from 3,4-dimethyl-5-vinylthiazolium iodide (**A**) (Scheme 1) and their use in thioesterification reactions.^[11] Continuing our work on expanding the scope of polymer-based organocatalytic systems, we screened a variety of reactions in the presence of **B**.



Scheme 1. Synthesis of poly(3,4-dimethyl-5-vinylthiazolium) iodide (B) from 3,4-dimethyl-5-vinylthiazolium iodide (A). AIBN = 2,2'-azobisisobutyronitrile.

Interestingly, we found that **A** and **B** were highly effective catalysts for the hydrothiolation of alkenes and alkynes under mild conditions. Herein, we report a simple and efficient protocol for the synthesis of linear and vinyl thioethers through the anti-Markovnikov addition of thiols to alkenes and alkynes by using N-heterocyclic carbene catalysts, **A** and **B**. Our catalysts were highly effective, even in the presence of air, and did not requires the use of metal complexes or free-radical initiators. High turnover numbers were observed in the presence of polymeric catalyst **B**. To the best of our knowledge, catalyst **B** is the first successfully recyclable organic polymer catalyst for the hydrothiolation reaction.

As a model reaction for hydrothiolation, we initially examined the reaction of styrene with thiophenol in the presence of polymeric **B** (1 mol%) for 60 min (Table 1). The reaction was highly sensitive to the medium and temperature. In CH_2CI_2 and toluene, the expected product was not formed (Table 1, entries 1 and 2). However, upon changing the solvent to DMF at 40 °C, the expected product was formed, albeit in low yield (14%; Table 1, entry 3). Increasing the amount of catalyst **B** to 2 mol% failed to produce any noticeable increase in yield (15%; Table 1, entry 4). To optimize the reaction conditions further, we screened a range of temperatures. No reaction was observed at 25 °C. Upon increasing the reaction temperature to 60 °C, the yield increased dramatically to 82%. However, a further increase in the temperature to 70 °C was not helpful in increasing the yield (81%; Table 1, entry 7). An increase in



Table 1. Optimization of the reaction conditions. ^[a] + HS - S							
	1a	2a	2a 3				
Entry	B [mol%]	Solvent	<i>T</i> [°C]	<i>t</i> [min]	Yield ^[b] [%]		
1	1	CH_2CI_2	40	60	N.R.		
2	1	toluene	40	60	N.R.		
3	1	DMF	40	60	14		
4	2	DMF	40	60	15		
5	1	DMF	25	60	N.R.		
6	1	DMF	60	60	82		
7	1	DMF	70	60	81		
8	1	DMF	60	90	96		
9	1	DMF	60	90	90 ^[c]		
10	0.01	DMF	60	90	58		
11	1	DMF	60	60	9 ^[d]		
[a] Conditions: 1a (1 mmol), 2a (1.1 mmol), B , in air. [b] Yield of isolated product; N.R. = no reaction. [c] Catalyst A was used. [d] Under a N_2 atmosphere.							

the reaction time to 90 min at 60 °C increased the yield of the product (96%; Table 1, entry 8). The optimum reaction conditions were found to involve the use of **B** (1 mol%), **1a** (1 mmol), and **2a** (1.1 mmol) in DMF (1 mL) at 60 °C for 90 min. Moreover, the catalytic activity of **B** was higher than that of monomeric **A** (96:90; Table 1, entry 8 vs. 9). The

amount of catalyst B could be lowered to 0.01 mol% (Table 1, entry 10). A turnover number of 5800 was observed for the catalyst under our optimized conditions.^[12] However, owing to experimental difficulties in measuring the turnover number with the small amount of catalyst B in our reaction system, the maximum turnover number was not investigated. We also examined the reusability of **B** in successive reactions (see the Supporting Information). For experimental feasibility, 5 mol % of B was used. Our catalytic system turned out to be quite robust and could be reused up to four times without any loss of catalytic activity (96, 97, 97, and 95% in runs 1, 2, 3, and 4, respectively). Interestingly, under a nitrogen atmosphere a poor yield (9%) was observed (Table 1, entry 11).

The hydrothiolation reaction under our standard reaction conditions tended to be quite clean and produced no significant side products. Next, the substrate scope of the hydrothiolation reaction with respect to the styrenes was examined under our optimized reaction conditions (Table 2). Using a standard thiol (thiophenol), reactions were performed with a variety of styrenes in the presence of both **A** and **B** as catalysts to compare their catalytic activities. For the substrates delivering products **3 aa**–i**a**, except for **3 ba** and **3 da**, higher yields were observed in the presence of polymeric catalyst **B** than in the presence of monomeric **A**. Substrates with an electron-withdrawing substituent (e.g., CF₃, F, Cl, and Br) reacted smoothly with the thiol to afford the corre-

sponding hydrothiolated products in good to high yields. If a methyl group was introduced to the α position (see products 3 ja and 3 ka), the yield decreased and catalyst A became more active than catalyst **B**. The yields observed in the presence of A were slightly higher than those in the presence of **B** (product 3 ja, 76 and 65%; product 3 ka, 77 and 70%). This observation might be explained by considering the feasibility of the substrate encountering the catalytically active sites. In polymeric catalyst **B**, the catalytically active sites are densely situated on the polymer backbone and are quite effective for the reaction with ordinary substrates. However, **B** is less effective than **A** in reactions involving sterically hindered substrates. The active sites in monomeric catalyst A might be more accessible to sterically demanding substrates than the active sites in B. It is interesting that catalysts **A** and **B** are complementary in terms of the hydrothiolation reaction of thiophenol with various styrenes. Among substrates having a halogen substituent, the substrate bearing a bromine atom showed the highest yield (products 3ga-ia: 78, 80, and 92%; products 3na and 3ma: 71 and 76%). 3-Chlorostyrene (91%) showed the highest yield among the 2-, 3-, and 4-chlorostyrenes. Interestingly, the formation of a β -nitrosulfide was observed in the reaction of (E)-(2-nitrovinyl)benzene (3 la).[13]

The scope of the reaction was then investigated further with a variety of thiols (Table 3). In general, high yields were ob-



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served for products **3 ab-ag**. However, as the aliphatic character of the thiols increased, the yields decreased (products **3 aeak**). Interestingly, higher yields were observed with monomeric catalyst **A** for most aliphatic thiols. For example, a poor yield (38%) was observed for pentanethiol in the presence

of **B** (product **3 aj**), but the yield increased to 62% in the presence of catalyst **A**. Upon using decane-1thiol as the substrate in the presence of **A**, the yield was still moderate at 50% (product **3 ak**). In the case of product **3 ad**, the yield was calculated by ¹H NMR spectroscopy, because of difficulties in separating the product from the reactant. Unfortunately, 2-aminobenzenethiol and 2-chlorobenzenethiol were unreactive under our reaction conditions. Overall, the substrate scope of our hydrothiolation process suggests that both steric and electronic factors may play a major role in the reaction.

To expand the scope of this reaction to alkynes, we investigated the hydrothiolation of ethynylbenzene with various thiols under our optimized reaction conditions (Table 4). It was encouraging to observe that the reactions went to completion within 30 min. In most cases, the (*E*)-vinyl sulfide was the predominant product. The regioselectivity of the hydrothiolation varied depending upon the substrate. Introduction of a substituent on the thiophenol led to a decrease in the *E/Z* ratio from 89:11 to 80:20 (products **5aa**, **5al**, and **5am**). If an electron-donating group $-NH_2$ was present on the thiophenol, the *Z* isomer was favored over the *E* isomer with a 91:9 ratio in a rather poor yield (31%). It seemed that as the chain length of the aliphatic thiol increased (products 5 ao, 5 aj, and 5 ak), both the yield and the selectivity for the E isomer increased. However, if dodecane thiol was used, poor regioselectivity was observed (E/Z =42:58). The best E/Z ratio was observed upon using decane thiol. A branched alkane thiol such as 2-ethylhexane-1-thiol gave the E isomer as a major product. If a substrate with a bulky substituent, such as (triisopropylsilyl)acetylene, was treated with thiophenol, a high E/Z ratio (product 5 pa; 90:10) was observed. In the reaction of 1,2-ethanedithiol, bis-hydrothiolation was observed, which resulted in the formation of 2-benzyl-1,3-dithiolane in 61% yield.^[14]

To gain some insight into the reaction mechanism, we performed the reaction in the presence of a common radical trap [i.e., 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), 1.21 equiv.]. No hydrothiolation product was formed in this case. Instead, 2,2,6,6-tetramethyl-1-[1-phenyl-2-(phenylthio)ethoxy]piperidine^[15] was obtained in a very low 9% yield (Scheme 2).

Our observation that the hydrothiolation reaction could be performed in air suggested di-

oxygen as a radical initiator in our reaction.^[16] Moreover, the formation of a product was not observed in the absence of catalyst **A**. This result suggests that catalyst **A** plays an important role in the reaction.



[a] Conditions: **4a** (1 mmol), **2** (1.1 mmol), **B** (1 mol%), DMF (1 mL), RT, 30 min. [b] Yield of isolated product. [c] The *E/Z* ratio was determined by analysis of the isolated product by ¹H NMR spectroscopy.

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To gain further information about the reaction, we prepared **C** and tested it as a catalyst in the hydrothiolation of styrene with thiophenol. Reaction in the presence of **C** led to the formation of diphenyl disulfide (42%) and phenethyl phenyl sulfide (43%) (Scheme 3). This result shows that the substituent at the C2 position of the thiazolium highly affects the reaction; furthermore, the yield of the hydrothiolation



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product obtained in the presence of catalyst **A** with a hydrogen atom at the C2 position was much higher than that obtained in the presence of catalyst **C** with a methyl group at the C2 position.^[17]

On the basis of our observations and those of others,^[18] we suggest that the reaction follows a radical mechanism (Figure 1). The key point of the hydrothiolation is the role of the thiazolium, which interacts with the thiyl radical; this re-



Scheme 2. Reaction of styrene with thiophenol in the presence of TEMPO.



Figure 1. Plausible reaction mechanism for the hydrothiolation reaction.



Figure 2. Energy profiles for the catalyzed and uncatalyzed thiol-ene reactions. For further details, please see the Supporting Information.

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sults in stabilization of the radical and enhances its addition to unsaturated c-c bonds.

The role of the thiazolium catalyst was confirmed by DFT calculations (Figure 2). The thiyl radical produced by the reaction with dioxygen is stabilized by catalyst **A** or **C** relative (stabilized by -10.53 and -7.86 kcal mol⁻¹ in the presence of **A** and **C**, respectively, relative to the free thiyl radical), and the addition of the thiyl radical to styrene in the presence of **A** shows the lowest activation energy barrier 12.01 kcal mol⁻¹ (TS_Cat.**A**). This is reflected in the high yield of the hydrothiolation product (90%). In the absence of catalyst **A** or **C**, no reaction is observed within 90 min. However, in the presence of **C** or without any catalyst, the energy of the transition state does not match the trend in the yield. Thus, stabilization of the thiyl radical seems to be critical to the hydrothiolation reaction.

In conclusion, we developed a robust method for the vinylthiazolium- or poly(vinylthiazolium)-catalyzed hydrothiolation of alkenes and alkynes. The reaction can be employed for both aliphatic and aromatic thiols. Our optimized reaction conditions afforded linear thioethers from both activated and unactivated alkenes with aliphatic and aromatic thiol partners in good to excellent yields under metal-free, additive-free, and open-air conditions. For most aromatic thiols, higher yields were observed in the presence of polymer catalyst **B**, but with aliphatic thiols, higher yields were generally observed with monomeric catalyst **A**. The polymeric catalyst showed a high turnover number (\approx 5800) and was recyclable.

Experimental Section

Procedure for the hydrothiolation of alkenes

A tube-type Schlenk flask equipped with a stirring bar was charged sequentially with catalyst **A** or **B** (2.6 mg, 0.01 mmol, 1 mol%), the styrene derivative (1 mmol), the thiol (\approx 1.1–2 mmol), and DMF (1 mL). The mixture was heated at 60 °C for 90 min. After the solution was cooled to room temperature, the solvent was evaporated under reduced pressure. Purification by flash chromatography (silica gel, *n*-hexane/ethyl acetate) afforded the thioether.

Procedure for the hydrothiolation of alkynes

A Schlenk flask equipped with a stirring bar was charged sequentially with catalyst **B** (2.6 mg, 0.01 mmol, 1 mol%), the acetylene derivative (1 mmol), the thiol (1.1 mmol), and DMF (1 mL). The mixture was stirred at room temperature for 30 min. The solvent was evaporated under reduced pressure, and purification by flash chromatography (silica gel, *n*-hexane/ethyl acetate) afforded the thioether.

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Hydrothiolation of Alkenes and Alkynes Catalyzed by 3,4-Dimethyl-5vinylthiazolium iodide and Poly(3,4dimethyl-5-vinylthiazolium) iodide Thio, thio, it's off to work we go! Highly selective anti-Markovnikov addition of thiols to unactivated alkenes and alkynes is demonstrated by using 3,4-dimethyl-5-vinylthiazolium iodide or its polymer, poly(3,4-dimethyl-5-vinylthiazolium) iodide, as a complementary catalyst. DFT calculations support a mechanism in which the thiazolium cation stabilizes a thiyl radical and enhances its reaction with unsaturated C–C bonds.