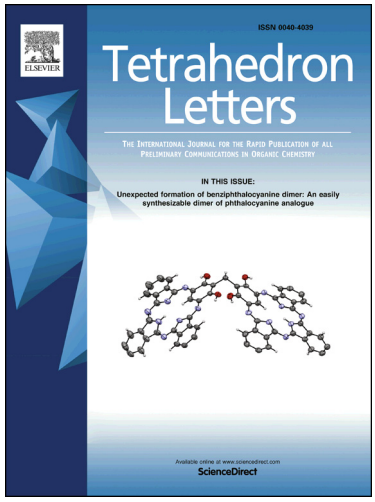

Sulfamic acid: an efficient and recyclable catalyst for the regioselective hydrothiolation of terminal alkenes and alkynes with thiols

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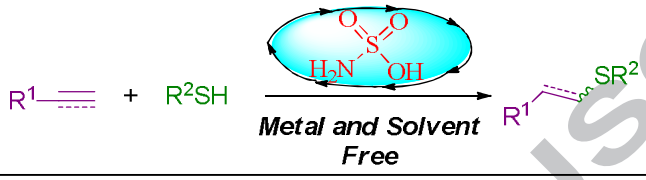

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Sulfamic acid: an efficient and recyclable catalyst for the regioselective hydrothiolation of terminal alkenes and alkynes with thiols

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ABSTRACT

Herein, we described a new method for the preparation of thioethers through hydrothiolation of alkenes and alkynes, using sulfamic acid as a reusable catalyst. Generally, this new methodology afforded the desired products in very good yields, under metal and solvent-free conditions. Furthermore, the catalyst was easily recovered and reused for further catalytic reactions without loss of activity.

1. Introduction

The generation of new carbon-sulfur bond has attracted considerable attention of synthetic organic chemists because organosulfur compounds have shown versatile properties, acting as valuable precursors in several transformations.[1,2] These kinds of organochalcogen compounds have also shown biological and pharmaceutical importance, for instance, it has play an important role showing therapeutic activities such as anticancer, antiviral and neuroprotective.[3]

Thioethers have become desirable target molecules once they have innumerous biological applications and proved to be versatile as synthetic intermediate especially for reactions involving multi-step transformations.[4] As a consequence of their synthetic and biological relevance, the development of several strategies to accomplish thioethers via anti-Markovnikov addition has been particularly investigated.[5]

The most appropriate and useful pathway for the preparation of thioethers with high atom efficiency is the hydrothiolation of alkenes and/or alkynes with thiols.[6] Usually, this method efficiently provides the desired products in high levels of stereo- and regio-selectivity either in the presence of radical inhibitor[7] or by using metal as a catalyst.[8] In this context, the selective preparation of thioethers via anti-Markovnikov addition has been achieved through the reaction of thiols with alkenes and alkynes, employing different transition-metals as catalysts,[9] including gold,[10] indium[11] and copper.[12]

Despite the good accomplishments, most of these methodologies present limitations such the use of toxic (e.g. carcinogenic) solvents, harsh conditions, as well as the use of expensive metal sources. Recently, we have prepared vinyl thioethers through the combination of nanocatalysis and solvent-free conditions.[13] Nevertheless, the development of new methods for the preparation of thioethers associated with metal-free conditions and easily recovered catalysts is still highly needed in terms of sustainability.

On the other hand, sulfamic acid (SA) has attracted particular attention due its unique properties such as non-volatile, non-corrosive, non-toxic, zwitterion behavior and high stability.[14] Furthermore, sulfamic acid is an inexpensive reagent and it is readily available from commercial suppliers. Consequently, SA has emerged as an important class of compound and it has been efficiently employed as catalyst in several transformations.[15] Particularly, the combination of sulfamic acid and solvent-free conditions can be considered an eco-friendly catalytic system and it has been successfully applied for a wide range of reactions,[16] including Michael addition,[17] Pechmann condensation[18] and multicomponent processes.[19]

Regardless the efficiency of sulfamic acid in a series of transformations, it has not been used as a catalyst for the

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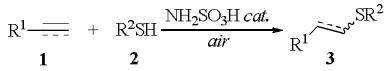
preparation of thioethers through hydrothiolation reaction. Therefore, in connection with our interest in environmental benign chemical processes,[20] a catalytic and metal-free approach for the hydrothiolation of alkenes and alkynes is described here (Scheme 1).



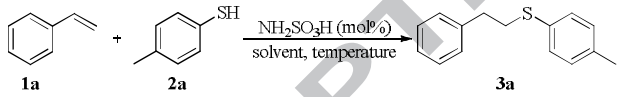
Scheme 1. Hydrothiolation of alkenes and alkynes with thiols.

2. Results and discussion

At first, we optimized the reaction parameters by using phenylstyrene **1a** and 4-methylbenzenethiol **2a** as model substrates (Table 1). Initially, the reaction was carried out in absence of catalyst by using toluene as solvent and desired thioether **3a** was obtained in very poor yield (entry 1). Then we evaluated the activity of sulfamic acid as a catalyst in this transformation (entries 2-4). In this regard, 20 mol% proved to be the best catalyst amount, affording the compound **3a** in reasonable yield (entry 4).The influence of different solvents was next investigated in detail. Nonetheless, no improvement in the reaction yield was observed when the nature of solvent was varied (entries 5-8).

To our delight, when the reaction was carried out in absence of any solvent the thioether **3a** was achieved with 74% yield (entry 9). Subsequently, we evaluated the influence of other parameters such as time and temperature (entries 10-13). On decreasing the reaction time from 1 to 0.5h a significant decrease in the yield of compound **3a** was observed (entry 10). However, no change in the yield value was detected when the reaction was carried out for 2h (entry 11). The reaction showed to be sensitive to any change in the temperature, affording the compound **3a** in lower yields (entries 12 and 13). In addition, no significant change in the chemical yield was observed when the reaction was carried out under inert atmosphere (entry 14).

Table 1
Optimization of the reaction conditions.[a]



Entry	NH_2SO_3H (mol%)	Solvent	Time (h)	T (°C)	Yield (%)
1	-	toluene	1	25	4
2	10	toluene	1	25	19
3	15	toluene	1	25	28
4	20	toluene	1	25	41
5	20	DMF	1	25	30
6	20	CH_2Cl_2	1	25	29
7	20	THF	1	25	12
8	20	EtOH	1	25	29
9	**20**	**-**	**1**	**25**	**74**
10	20	-	0.5	25	18
11	20	-	2	25	74
12	20	-	1	0	10
13	20	-	1	50	29
14	20	-	1	25	69[b]

[a]Reaction was performed by employing styrene **1a** (0.6 mmol), 4-netylbenzenethiol **2a** (0.5 mmol), solvent and catalyst.

[b] The reaction was carried out under argon atmosphere.

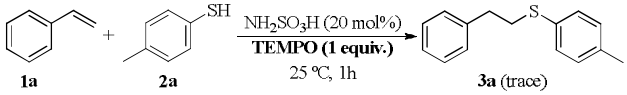
Once defined the best reaction conditions, we have focused in the study of the scope and limitations of our protocol (Table 2).[21] Generally, 4-methylbenzenethiol reacted very well with styrene derivatives, furnishing the corresponding products in very good yields (entries 1-3). For instance, when 4-methoxystyrene **1d** was treated with 4-methylbenzenethiol the product **3c** was obtained in 82% yield (entry 3). However, a decrease in the reaction yield was observed when 4-chlorobenzenethiol **2b** was employed as a organosulfur source (entry 4). Also, benzenethiol **2c** reacted smoothly with styrene, affording the corresponding product in satisfactory yield (entry 5). Aliphatic thiols were not applicable substrates under optimized conditions (entries 6 and 7). Moreover, the reaction failed when dihydropyran was employed as substrate (entry 8).

In addition, the protocol was applied for the synthesis of thioethers starting from aliphatic alkenes, containing different functional groups such as alcohol and ester (entries 9 and 10). In fact, the reaction between allylic alcohol and 4-methylbenzenethiol resulted in the formation of desired product in 66% yield (entry 9).

Next, we also attempted to synthesize a wide range of vinyl thioethers by treating different thiols with terminal alkynes (Table 2, entries 11-19). To our delight, when 4-methylbenzenethiol **2a** was treated with phenylacetylene **1h** the desired product **3k** was isolated in 89% yield (entry 11). However, thiophenol and 4-chlorobenzenethiol were less reactive substrates when treated with phenylacetylene, affording the corresponding products in lower yields but with higher stereoselectivity (entries 12 and 13). Furthermore, the employment of aliphatic thiols allowed the preparation of desired products in high level of stereoselectivity with lower chemical yields values (entries 14 and 15).

Different terminal alkynes were also evaluated as substrates in this transformation (Table 2, entries 16-19). Electronic effects from substituents attached to the *para* position of aromatic ring seem to show a remarkable influence in the hydrothiolation of alkynes (entries 16 and 17). Noteworthy, when an acetylene with a methyl group at the *para* position of the aromatic ring was employed, the corresponding vinyl thioether **3p** was delivered in 88% yield with a *Z*:*E* ratio of 82:18. Nonetheless, aliphatic alkynes were not appropriate substrates for this hydrothiolation process (entries 18 and 19). In addition, we also carried out the reaction under catalyst-free condition (entry 20). However, the desired product was obtained in very poor yield and stereoselectivity, highlighting the efficiency of sulfamic acid as a catalyst in this kind of transformation.

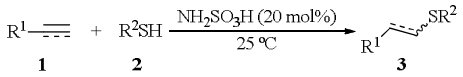
The results showed in Table 2 suggest that the hydrothiolation process is affected for the substituents present in the structures of all substrates. The unsatisfactory reaction behavior observed in some experiments could be associated with the lack of stability/reactivity of some radical species,[22] which are probably involved in the product formation. Thus, in order to get some insights into the mechanism of the reaction a control experiment was realized in the presence of (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (TEMPO). In this reaction only a trace amount of desired product **3a** was observed, which might indicate a possible reaction pathway (Scheme 2).



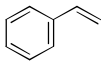
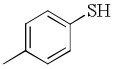
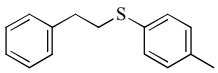
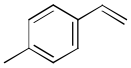
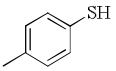
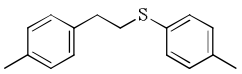
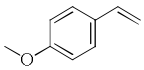
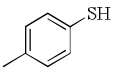
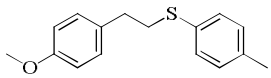
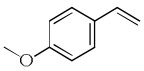
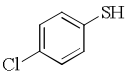
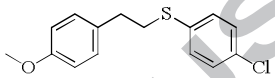
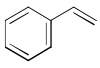
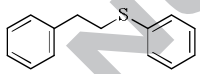
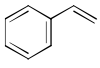
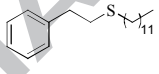
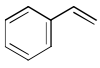
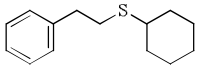
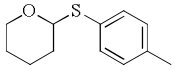
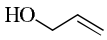
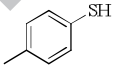
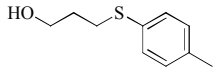
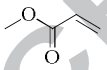
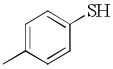
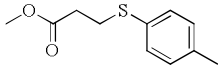
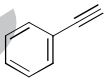
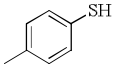
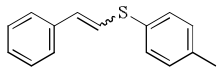
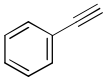
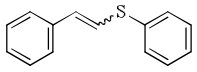
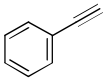
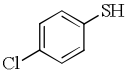
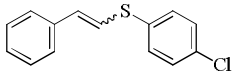
Scheme 2. Hydrothiolation in the presence of TEMPO.

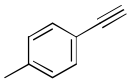
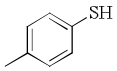
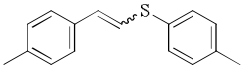
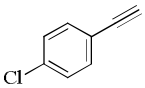
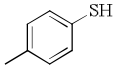
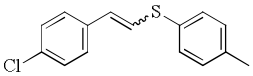
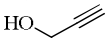
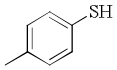
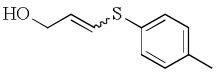
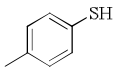
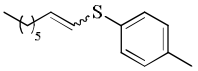
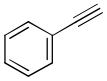
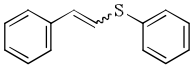
Based on our studies and in accordance to previous reports,[6a-b, 8a] a plausible reaction pathway is shown in Scheme 3. We believe that initially the thiyl radical **4** is formed in the reaction medium.

Table 2
Scope of the hydrothiolation reaction of terminal alkenes/alkynes **1** with thiols **2**.[a]



1 **2** **3**

Entry	Alkene/Alkyne **1**	Thiol **2**	Product **3**	Time (h)	Yield % (*Z*:*E*)[b]
1	 **1a**	 **2a**	 **3a**	1	74
2	 **1b**	 **2a**	 **3b**	1	71
3	 **1c**	 **2a**	 **3c**	1	82
4	 **1d**	 **2b**	 **3d**	1	58
5	 **1a**	 **2c**	 **3e**	5	60
6	 **1a**	 **2d**	 **3f**	1	---
7	 **1a**	 **2e**	 **3g**	1	trace
8	 **1e**	 **2a**	 **3h**	6	---
9	 **1f**	 **2a**	 **3i**	1	66
10	 **1g**	 **2a**	 **3j**	1	21
11	 **1h**	 **2a**	 **3k**	1	89 (54:46)
12	 **1h**	 **2c**	 **3l**	5	59 (13:87)
13	 **1h**	 **2b**	 **3m**	1	46 (71:29)
14	**1h**	**2d**	**3n**	2	20 (80:20)
15	**1h**	**2f**	**3o**	2	24 (83:17)

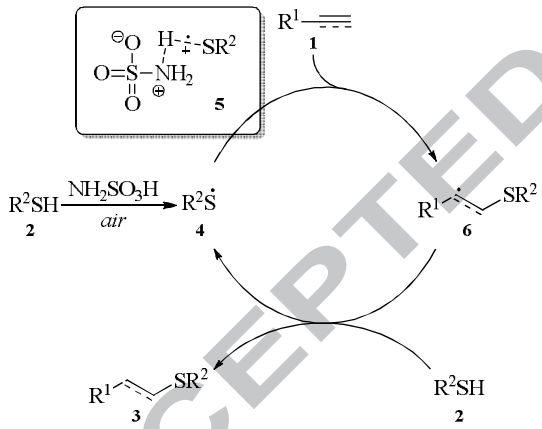
16	 **1i**	 **2a**	 **3p**	1	88 (82:18)
17	 **1j**	 **2a**	 **3q**	1	73 (67:33)
18	 **1k**	 **2a**	 **3r**	5	trace
19	 **1l**	 **2a**	 **3s**	5	---
20	 **1h**	 **2c**	 **3l**	5	14 (44:56)

[a] The reaction was carried out using alkene/alkyne **1** (0.6 mmol), thiol **2** (0.5 mmol) and NH_2SO_3H (20 mol%) at 25 °C, under air.

[b] Determined by ^1H NMR spectroscopy.

[c] The reaction was carried out in absence of catalyst.

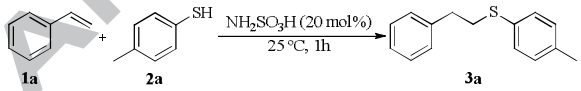
This radical could be stabilized by the interaction with the catalyst furnishing **5**, which is analogous specie to the proposed model reported by Chung and co-workers.[6a] Subsequently, this specie would interact with alkene/alkyne **1** giving the intermediate **6**. Finally, this radical specie reacts with thiol **2**, furnishing the corresponding product **3**.



Scheme 3. A plausible reaction pathway.

Furthermore, we also evaluated the possibility to recover and reuse the sulfamic acid employed in the reactions. Therefore, after carried out the reaction under optimized conditions, the catalyst was recovered by simple filtration and reused for further reactions. Notably, the sulfamic acid conserved its catalytic activity up to fourth cycle, furnishing the respective product in very good yield (Figure 1).

In summary, we effectively established a metal and solvent free protocol for the preparation thioethers, using sulfamic acid as a recyclable catalyst, at room temperature under air. Generally, this new methodology afforded the corresponding products in very good yields with high selectivity. Most importantly, sulfamic acid proved to be a highly effective catalyst for the hydrothiolation of alkenes and alkynes and it was recovered and recycled up to four cycles without significant loss of activity.



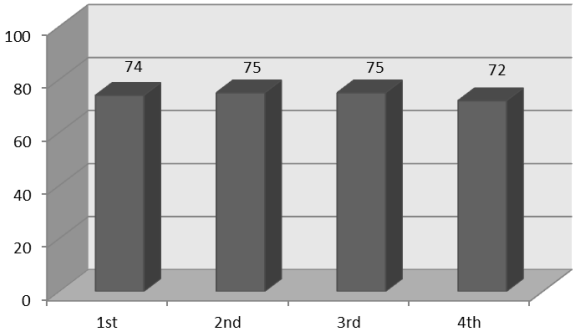


Figure 1. Recyclability of the catalyst.

Acknowledgments

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21. *General procedure for the synthesis of thioethers:* Thiol (0.5 mmol) and alkene or alkyne (0.6 mmol) were placed into a tube containing sulfamic acid (20 mol%). The mixture was magnetically stirred during 1 hour at room temperature. Then, the reaction was quenched with water and the aqueous layer was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered, and the solvent and volatiles were completely removed under vacuum to give the crude product. Purification by flash chromatography on silica, eluting with a mixture of ethyl acetate/hexane (1:99), furnished the desired thioeter.
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Supplementary Material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016

Highlights

- Regioselective hydrothiolation of alkenes and alkynes with thiols.
- Metal- and solvent-free method for efficient preparation of thioethers.
- The catalyst was easily recovered and reused for further catalytic reactions without loss of activity.