Tetrahedron Letters 58 (2017) 3777–3781

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

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

Clarissa Helena Rosa [a], Maura Luise B. Peixoto [a], Gilber Ricardo Rosa [a], Benhur Godoi [b], Fábio Zazyki Galetto [c], Marcelo Gonçalves Montes D'Oca [a], Marcelo Godoi [a,*]

[a] *Escola de Química e Alimentos, Universidade Federal do Rio Grande, Campus Santo Antônio da Patrulha, RS, Brazil*
[b] *Núcleo de Síntese, Aplicação e Análise de Compostos Orgânicos e Inorgânicos, Universidade Federal da Fronteira Sul, Campus Cerro Largo, RS, Brazil*
[c] *Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, Brazil*

ARTICLE INFO

Article history:
Received 3 July 2017
Revised 17 August 2017
Accepted 21 August 2017
Available online 23 August 2017

Keywords:
Sulfamic acid
Hydrothiolation
Metal-free
Catalysis
Organosulfur

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.

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 multistep 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]

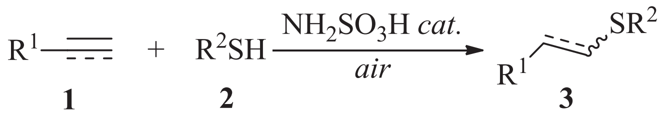
The most appropriate and useful pathway for the preparation of thioethers with high atom efficiency is the hydrothiolation of alkenes and/or alkynes with thiols.[6] Usually, this method efficiently provides the desired products in high levels of stereo- and regioselectivity either in the presence of 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]

* Corresponding author.
E-mail address: marcelogodoi@furg.br (M. Godoi).

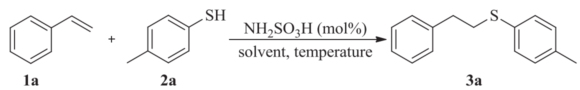
http://dx.doi.org/10.1016/j.tetlet.2017.08.051



Scheme 1. Hydrothiolation of alkenes and alkynes with thiols.

Regardless the efficiency of sulfamic acid in a series of transformations, it has not been used as a catalyst for the preparation of thioethers through hydrothiolation reaction. Therefore, in connection with our interest in environmental benign chemical

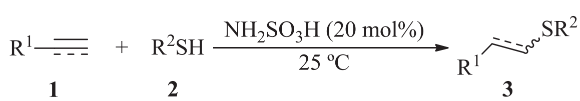
Table 1
Optimization of the reaction conditions.[a]

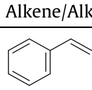
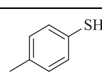
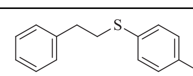
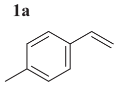
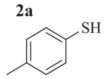
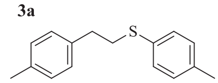
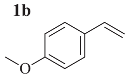
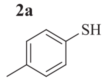
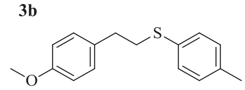
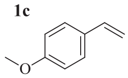
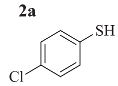
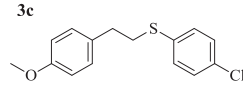
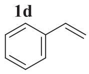
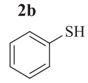
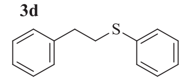
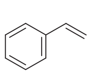
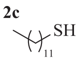
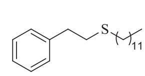


Entry	NH_2SO_3H (mol%)	Solvent	Time (h)	T (°C)	Yield (%)
1	–	toluene	1	25	4
2	10	toluene	1	25	19
3	15	toluene	1	25	28
4	20	toluene	1	25	41
5	20	DMF	1	25	30
6	20	CH_2Cl_2	1	25	29
7	20	THF	1	25	12
8	20	EtOH	1	25	29
9	20	–	1	25	74
10	20	–	0.5	25	18
11	20	–	2	25	74
12	20	–	1	0	10
13	20	–	1	50	29
14	20	–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

[a] Reaction was performed by employing styrene **1a** (0.6 mmol), 4-methylbenzenethiol **2a** (0.5 mmol), solvent and catalyst.
[b] The reaction was carried out under argon atmosphere.

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



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	–