



Rice straw ash extract, an efficient solvent for regioselective hydrothiolation of alkynes

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Abstract

Herein, we describe a simple and inexpensive protocol for the hydrothiolation of alkynes. In this context, water extract of rice straw ash (WERSA) has been proven to be a green, mild and efficient solvent for the preparation of vinyl thioethers. Generally, it was found that alkyne and thiol derivatives were excellent reaction partners, producing the corresponding products with good yields and good stereoselectivity with the predominant formation of the *Z* isomer. Moreover, WERSA was recovered and reused for further catalytic reactions without a significant loss of activity.

Keywords WERSA · Hydrothiolation · Alkynes · Alkenes · Thiols · Agro-waste

Introduction

Water extract of agro-waste ashes (AWEs) have recently attracted considerable attention in modern organic synthesis since these solvents are non-toxic, inexpensive and biodegradable (Sarmah et al. 2017). In this context, AWE have been successfully used as green catalytic media in several organic transformations (Konwar et al. 2016; Chia et al. 2018), such as the Suzuki–Miyaura (Boruah et al. 2015a, b; Sarmah et al. 2016) and Sonogashira reactions (Dewan et al. 2016). More specifically, water extract of rice straw ash (WERSA) has become the most powerful solvent for organic synthesis (Saikia et al. 2015). This solvent is primarily constituted by SiO₂ (74.31%), K₂O (11.30%), P₂O₅ (2.65%), MgO (1.89%), Na₂O (1.85%), CaO (1.61%), Al₂O₃ (1.40%), Fe₂O₃ (0.73%) and TiO₂ (0.02%) (Jenkins et al. 1996). The unique properties of WERSA make this solvent particularly

valuable in a series of transformations (Mahanta et al. 2016; Boruah et al. 2015a, b), including the Dakin (Saikia and Borah 2015) and Henry reactions (Surneni et al. 2016).

Furthermore, organosulfur derivatives have become a valuable class of compounds that are useful intermediates in the preparation of target molecules with synthetic (Silveira et al. 2017) as well as biological applications (Li et al. 2013). In this regard, vinyl thioethers have been efficiently applied in several transformations (Palomba et al. 2016), including total synthesis (Pearson et al. 2004). Due to the extremely wide range of applications of vinyl thioethers, several research groups have reported suitable methodologies for obtaining vinyl thioethers (Singh et al. 2013; Rodygin et al. 2017). For example, these compounds can be prepared through metal-catalyzed cross-coupling reactions of vinyl halides with either thiols (Reddy et al. 2009) or diorganyl disulfides (Kundu et al. 2013; Gonçalves et al. 2013). However, the most useful and atom-economical method for the preparation of vinyl thioethers is the hydrothiolation of alkynes (Strydom et al. 2017). Among these, catalytic hydrothiolation techniques have emerged as a conveniently alternative to afford vinyl thioethers which can be obtained by either anti-Markovnikov- or Markovnikov-type addition (Malyshev et al. 2006; Beletskaya and Ananikov 2007, 2011). Generally, this strategy can yield the respective products at different levels of stereo- and regioselectivity under different conditions (Dondoni and Marra 2014; Palacios et al. 2016). In particular, the selective preparation of vinyl thioethers through the anti-Markovnikov pathway has received

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special attention and has been prominently described in the literature (Kondoh et al. 2005; Liao et al. 2013; Silva et al. 2008; Chun et al. 2016). In this context, vinyl thioethers have been efficiently obtained by transition-metal-catalyzed reactions (Modem et al. 2016; Zhao et al. 2012), for instance, using iron (Rocha et al. 2017), copper (Riduan et al. 2012; Yang and Rioux 2014; Trostyanskaya and Beletskaya 2012), indium (Sarma et al. 2012) and gold (Corma et al. 2010).

In spite of these advances, most of these protocols have different drawbacks such as air sensitivity and the use of expensive metals and toxic solvents. Very recently, we have reported an effective method for the hydrothiolation of alkenes and alkynes under more green conditions (Rosa et al. 2017). Nevertheless, the development of an alternative method for obtaining vinyl thioethers with high selectivity is still highly desirable.

Despite the high effectiveness of WERSA in a wide range of reactions, to the best of our knowledge, it has not been applied as a solvent in the hydrothiolation transformations. Thus, herein, we report a straightforward and useful methodology for the synthesis of vinyl thioethers using WERSA as a natural feedstock solvent (Scheme 1).

Experimental

General procedure

Thiol **1** (0.5 mmol) and terminal acetylene **2** (0.6 mmol) were placed in a round-bottom flask, followed by the addition of the solvent (1 mL). The mixture was stirred at room temperature for 2 h, and the progress of the reaction was monitored by thin-layer chromatography (TLC). After the reaction was completed, the product was extracted with diethyl ether and water (3 × 5 mL). The organic phase was dried over MgSO₄ and filtered, and the volatiles were completely removed under a vacuum. The crude product was purified by column chromatography with a mixture of ethyl acetate/hexane (01:99) to afford the desired vinyl thioether **3**.

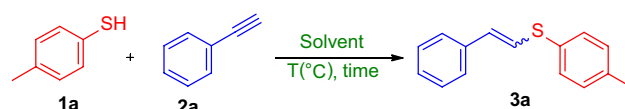
Preparation of WERSA 1 g of rice straw ash was suspended in 10 mL of distilled water in an Erlenmeyer and it was stirred for 1 h at room temperature. Subsequently, this mixture was filtered through a sintered glass crucible and the filtrate was used as WERSA. **Recyclability experiments** After completion of the synthesis, the reaction mixture was extracted with diethyl ether (5 × 2 mL) and the organic phase, containing the crude

product, was separated from WERSA. The residue of WERSA was reused directly for the next experiment.

Results and discussion

To optimize the reaction conditions, 4-methylbenzenethiol **1a** and phenylacetylene **2a** were selected as standard substrates (Table 1). Initially, the reaction was carried out under inert atmosphere conditions in the presence of water extract of rice straw ash (WERSA), affording thioether **3a** with a 69% yield and very poor stereoselectivity (entry 1). However, when the reaction was carried out in the air

Table 1 Optimization of the reaction conditions



Entry	Solvent	Time (h)	Temperature (°C)	Yield ^a (%)	(Z:E) ^b
1	WERSA	1	25	69	51:49 ^c
2	WERSA	1	25	89	76:24
3	WERSA	1	0	75	85:15
4	WERSA	1	50	91	87:13
5	WERSA	1	100	91	82:18
6	WERSA	2	25	93	83:17
7	WERSA	3	25	89	82:18
8	WERSA	0.5	25	76	86:14
9	WERSA	2	50	96	80:20
10	WERSA	2	100	89	56:44
11	Toluene	2	25	51	85:15
12	THF	2	25	72	62:38
13	DCM	2	25	80	69:31
14	CH ₃ CN	2	25	76	60:40
15	H ₂ O ^d	2	25	64	75:25
16	H ₂ O ^e	2	25	85	86:14
17	WEB	2	25	90 ^f	75:25
18	WEPAB	2	25	80	84:16

The reaction was performed by using 4-methylbenzenethiol **1a** (0.5 mmol), phenylacetylene **2a** (0.6 mmol) and solvent

WERSA water extract of rice straw ash; THF tetrahydrofuran; DCM dichloromethane; WEB water extract of banana peel ash; WEPAB water extract of papaya peel ash

^aYields for isolated products

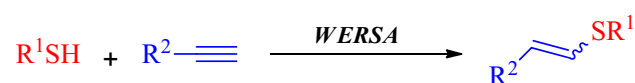
^bDetermined by ¹H NMR spectroscopy

^cThe reaction was carried out under inert atmosphere

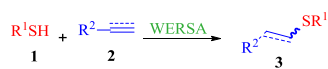
^dUnder acidic conditions

^eUnder basic conditions, in the presence of K₂CO₃

^fThe formation of PhSSPh as a by-product was detected in the crude



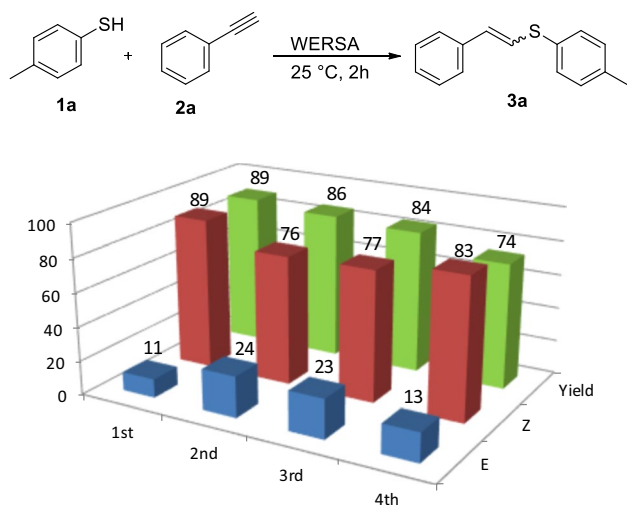
Scheme 1 Hydrothiolation of alkynes by water extract of rice straw ash (WERSA)

Table 2 Scope of the hydrothiolation reaction of terminal thiols **1** with alkynes **2**

Entry	Thiol	Alkyne/Alkene	Product	Time (h)	Yield ^a %(Z:E) ^b
1				2	93 (83:17)
2				2	70 (68:32)
3				3	54 (88:12)
4				3	92 (81:19)
5				2	47 (66:34)
6				4	71 (87:13)
7				4	32 (81:19)
8				2	96 ^c (71:29)
9				2	65 (68:32)
10				2	56 (93:07)
11				7	Traces
12				4	Traces
13				2	42
14				2	76

Table 2 (continued)

Reaction conditions: terminal thiol **1** (0.5 mmol), alkyne **2** (0.6 mmol) in WERSA (1 mL) at room temperature
^aYields for isolated products
^bDetermined by ¹H NMR spectroscopy
^cThe reaction was carried out at 50 °C

**Fig. 1** Recyclability of water extract of rice straw ash (WERSA)

atmosphere, the desired product was achieved with an 89% yield and a *Z/E* ratio of 76:24 (entry 2). Next, we investigated the most appropriate temperature for the reaction. Room temperature proved to be the best choice since no improvement in the chemical yield of **3a** was achieved when this parameter was modified (entries 3–5).

After identifying the best temperature, we then evaluated the influence of the reaction time on the reaction system (entries 6–8). A screening of this parameter revealed that 2 h was the best option, furnishing the desired product with a 93% yield and *Z/E* ratio of 83:17 (entry 6). Having determined the optimal time and temperature, the influence of several solvents was next investigated in detail (entries 11–16). However, no enhancement in the yield value of product **3a** was achieved in the presence of any other solvent. It was also observed that the basic nature of WERSA (pH 12) seems to be essential for this hydrothiolation reaction, since better results were obtained under alkaline conditions (compare entries 6, 15 and 16).

Furthermore, we also evaluated the activity of different ash water extracts such as water extract of banana peel ash (WEB) and water extract of papaya peel ash (WEPAB). However, a slight decrease in the yield value of vinyl thioether **3a** was observed by using these ash water extract variants (entries 17 and 18).

Having optimized the reaction conditions, we then evaluated the substrate scope using different thiols **1** and alkynes

2 (Table 2). Initially, we focused particularly on the influence of several aromatic thiols on the reaction (entries 1–5). Regarding the electron effects, it was found that the reaction proceeded efficiently in the presence of electron-donating groups, affording the respective products with good yields and appreciable stereoselectivity (entries 1 and 2). Nevertheless, when an aromatic thiol containing a withdrawing group attached at the *para* position of the aromatic ring was used, a significant decrease in the yield value was observed (entry 3). To our delight, it was also observed that thiophenol reacted very smoothly with phenyl acetylene, furnishing the corresponding product **3d** with a 92% yield and *Z/E* ratio of 81:19 (entry 4). Regarding the steric effects, it was observed that steric hindrance at the ortho-substituted thiol affected the reaction course since compound **3e** was achieved with a lower yield and stereoselectivity under optimized conditions (entry 5).

Furthermore, we also investigated whether the reaction could be applied for the preparation of vinyl thioethers starting from aliphatic thiols (entries 6–7). Gratifyingly, when cyclohexanethiol was used, product **3f** was obtained with a 71% yield and a *Z/E* ratio of 87:13 (entry 6). However, a decrease in the yield value was observed when 1-dodecanethiol was employed as the sulfur source (entry 7).

Next, we evaluated the influence of different alkynes on the reaction system (entries 8–13). Generally, 4-methylbenzenethiol reacted well with different alkynes derivatives, furnishing the corresponding products with satisfactory yields and reasonable stereoselectivities. It was found that terminal alkynes bearing electron-releasing substituents were less reactive than their withdrawing analogs (entries 8–9). For instance, when 1-chloro-4-ethynylbenzene **2b** was treated with 4-methylbenzenethiol, the desired product **3h** was achieved with a 96% yield and a *Z/E* ratio of 71:29 (entry 8). However, when a phenylacetylene derivative containing a methyl group at the *para* position was used, the respective product was obtained with a lower yield and stereoselectivity (entry 9).

However, 3-ethynylanisole **2d** reacted smoothly with 4-methylbenzenethiol, affording the respective product with a reasonable yield and very high stereoselectivity (entry 10). Nevertheless, the reaction was not applicable for the hydrothiolation of aliphatic alkynes since only traces of the products **3k** and **3l** were observed under similar conditions (entries 11 and 12).

It is well recognized that the preparation of thioethers through the hydrothiolation of alkenes via the anti-Markovnikov addition has also received particular attention and has been well described (Banerjee et al. 2010). Thus, inspired by the results obtained in the preparation of vinyl thioethers, we also attempted to treat thiols with alkenes under similar conditions (entries 13–14). Gratifyingly, the reaction of phenylstyrene with thiols **1a** and **1c** afforded the corresponding products with reasonable yields (entries 13–14).

To investigate whether the present approach is an environmentally benign strategy for the preparation of vinyl thioethers, we also studied the recyclability of WERSA (Fig. 1).

Therefore, after carrying out the reaction under optimized conditions, the solvent was easily recovered from the reaction media and reused for further transformations. Notably, WERSA conserved its activity up to the fourth cycle, furnishing the respective thioether **3a** with a very good yield and high stereoselectivity (Fig. 1).

Conclusion

In summary, we successfully developed an efficient and easy-to-perform method for obtaining vinyl thioethers by the hydrothiolation of alkynes with thiols using WERSA as a recyclable solvent. Generally, the corresponding products were obtained with good to excellent yields and good stereoselectivity. Remarkably, WERSA was easily recovered from the reaction media and reused for up to four cycles without a significant loss of activity. We believe that the chemistry described herein represents an environmentally friendly alternative for the hydrothiolation of alkynes. Studies on elucidating the mechanism of this transformation are still in progress in our laboratory.

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