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SHORT COMMUNICATION

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$CuSO_4 \cdot 5H_2O$-*H*-Phosphonate-Catalyzed Intermolecular C–S Bond Formation: Synthesis of (*E*)-Vinyl Alkylsulfones from Alkynes and DMSO

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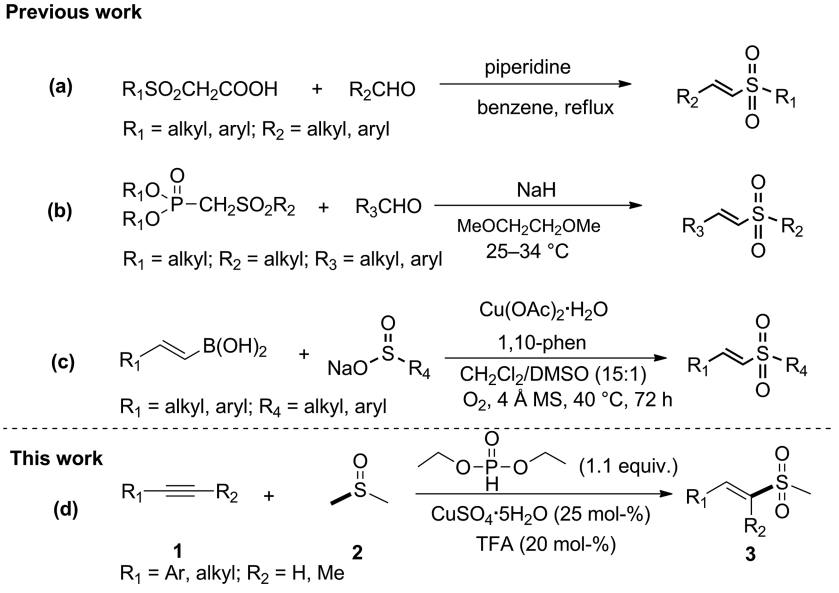
A $CuSO_4 \cdot 5H_2O$-*H*-phosphonate-catalyzed synthesis of (*E*)-vinyl alkylsulfones from alkynes and widely available DMSO was developed. The present protocol provides an alternative approach to various vinyl sulfones, with the advantages of cheap catalysts, readily available starting materials, operational simplicity and high stereo- and regioselectivity.

Introduction

Vinyl sulfones are widely used as building blocks in synthetic organic chemistry. For example, the chemical versatility of the sulfone moiety enables these compounds to undergo highly stereoselective nucleophilic conjugate additions[1] and cycloadditions,[2] epoxidation,[3] and reduction reactions.[4] Vinyl sulfones have been used for the total synthesis of natural products.[5] Furthermore, the sulfone group can be removed at the end of a synthetic sequence by a variety of reductive, alkylative, or oxidative methods.[6] Moreover, in medicinal chemistry, vinyl sulfones represent a new class of inhibitors of enzymes, such as cysteine proteases,[7] dipeptidyl peptidase I (DPPI), and transpeptidase.[8] Because of their wide applications, various methodologies for the synthesis of vinyl sulfones have been developed. The traditionally available methodologies for the synthesis of vinyl sulfones mainly include the following: 1) Knoevenagel condensations of aldehydes with sulfon-



Scheme 1. Methods for the synthesis of vinyl sulfones.

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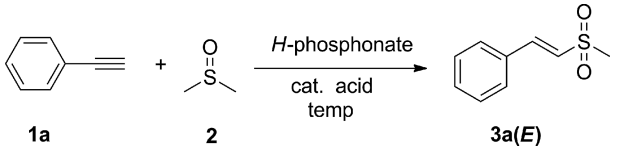
ylacetic acids (Scheme 1-a),[9] 2) Wittig reactions of carbonyl compounds and sulfonylphosphones (Scheme 1-b),[10] 3) β-elimination of selenosulfones,[11] and 4) oxidation of the corresponding vinyl sulfides.[12] A number of alternative methods towards vinyl sulfone synthesis have also been developed, such as the cross-coupling of sulfinate salts with vinyl triflates, vinyl bromides, or alkenylboronic acids catalyzed by Cu or Pd catalysts (Scheme 1-c).[13] However, most of these methods suffer from some limitations, such as inaccessible starting materials, tedious procedures, relatively harsh reaction conditions, or generation of large amounts of unwanted byproducts. Recently, copper- or palladium-catalyzed hydrosulfonylations of alkynes with sulfinic acids or sodium sulfinates were developed.[14] Very recently, a copper-catalyzed aerobic decarboxylative sulfonylation of alkenyl carboxylic acids with sodium sulfinates was developed by Guo and co-workers.[15] A synthesis of vinyl sulfones, by means of Cu^{I}-catalyzed aerobic oxidative N–S bond cleavage of sulfonyl hydrazides, followed by cross-coupling reactions with alkenes and aromatic compounds, was also described by Jiang and co-workers.[16] Moreover, the synthesis of α-substituted vinyl sulfones, rather than vinyl sulfones mentioned above, from terminal alkynes and sulfinic acids by gold-catalyzed intermolecular C–S bond formation was carried out by Shi and co-workers.[17] Herein, we report an efficient method for the synthesis of vinyl sulfones from alkynes and DMSO, by using a cheap, easily available $CuSO_4·5H_2O$-*H*-phosphonate catalytic system (Scheme 1-d). To the best of our knowledge, it is the first example of using widely available DMSO together with relatively benign and inexpensive $CuSO_4·5H_2O$ to prepare vinyl sulfones.

Results and Discussion

Initially, phenylacetylene (**1a**) and DMSO (**2**) were chosen as the substrates to optimize the reaction conditions. The screening results are shown in Table 1. The influences of four kinds of *H*-phosphonates on the model reaction were first investigated (Table 1, Entries 1–4). The reaction of **1a** (1 equiv.) with **2** (1.0 mL) in the presence of $CuSO_4·5H_2O$ (25 mol-%), trifluoroacetic acid (TFA, 0.2 equiv.) at 120 °C, and various *H*-phosphonates: diethyl *H*-phosphonate (DEPH), diisopropyl *H*-phosphonate, dipropyl *H*-phosphonate, or diphenyl *H*-phosphonate

Table 1. Optimization of the reaction conditions.[a]



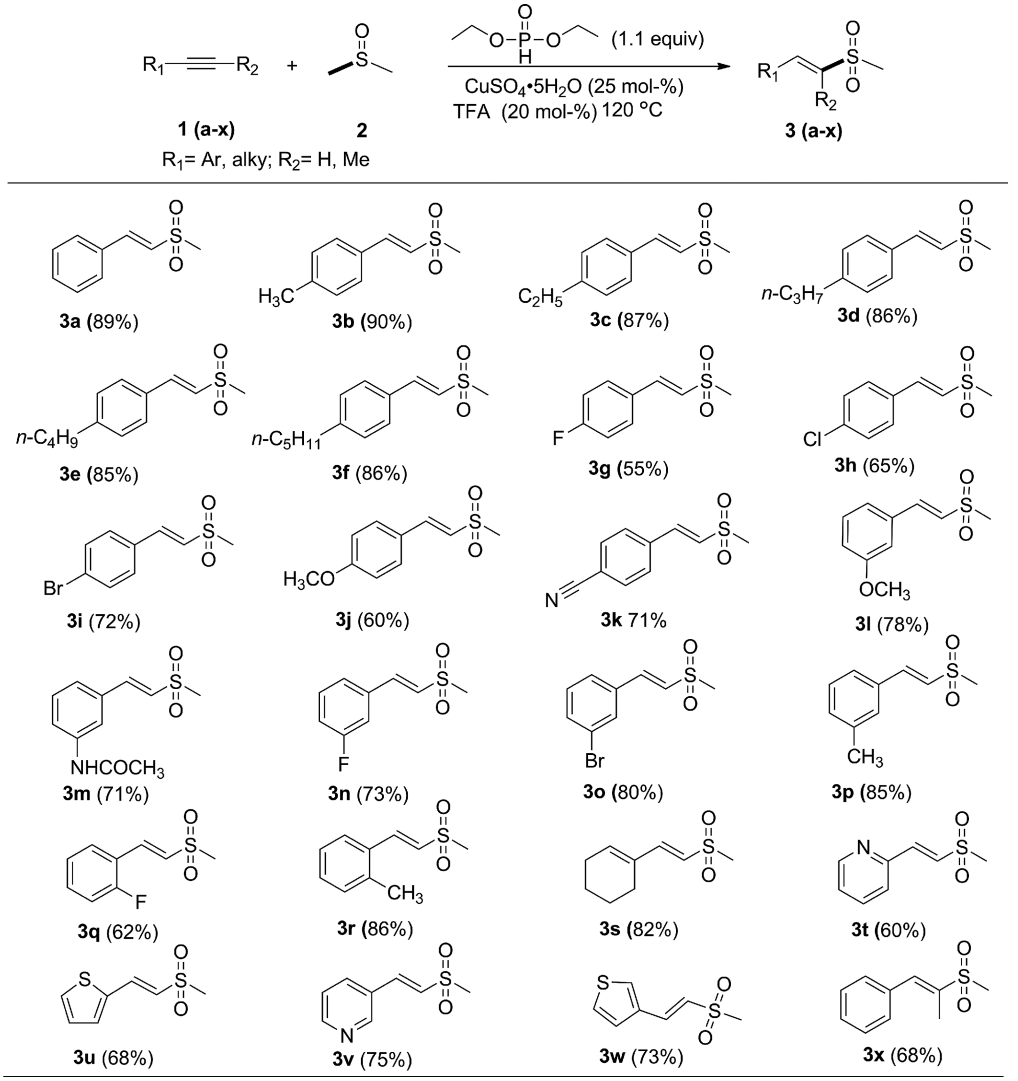
1a **2** **3a(*E*)**

Entry	Cat (mol-%)	*H*-phosphonate $HPO(OR)_2$ R (equiv.)	Acid (equiv.)	Solvent	*T* [°C]	Yield [%] (*E*)[b]
1	**$CuSO_4·5H_2O$ (25)**	**CH_2CH_3 (1.1)**	**TFA (0.2)**	**DMSO**	**120**	**89**
2	$CuSO_4·5H_2O$ (25)	$CH(CH_3)_2$ (1.1)	TFA (0.2)	DMSO	120	86
3	$CuSO_4·5H_2O$ (25)	$CH_2CH_2CH_3$ (1.1)	TFA (0.2)	DMSO	120	85
4	$CuSO_4·5H_2O$ (25)	C_6H_5 (1.1)	TFA (0.2)	DMSO	120	32
5	$CuSO_4·5H_2O$ (25)	–	TFA (0.2)	DMSO	120	NR
6	$CuSO_4·5H_2O$ (25)	CH_2CH_3(0.5)	TFA (0.2)	DMSO	120	38
7	CuBr (25)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	120	trace
8	CuI (25)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	120	trace
9	$Cu(OAc)·2H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	120	50
10	$NiCl_2·6H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	120	NR
11	$CuSO_4·5H_2O$ (10)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	120	24
12	$CuSO_4·5H_2O$ (40)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	120	86
13	$CuSO_4·5H_2O$ (60)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	120	84
14	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	80	42
15	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	100	76
16	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	DMSO	140	85
17	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	AcOH (0.2)	DMSO	120	52
18	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	$(CH_3)_3CO_2H$ (0.2)	DMSO	120	69
19	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TsOH (0.2)	DMSO	120	NR
20[c]	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	DMF	120	trace
21[c]	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	toluene	120	trace
22[c]	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	1,4-dioxane	120	trace
23[c]	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.2)	$(CH_3CO)_2O$	120	trace
24	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	TFA (0.1)	DMSO	120	45
25	$CuSO_4·5H_2O$ (25)	CH_2CH_3 (1.1)	–	DMSO	120	30

[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mL), dialkyl *H*-phosphonate (0–1.1 equiv.), catalyst (10–60 mol-%) and TFA (0–0.2 equiv.) at 120 °C for 10 h. [b] Isolated yields. [c] DMSO (2.5 mmol) in solvent (1.0 mL).

(1.1 equiv.) afforded the desired product (*E*)-[2-(methyl-sulfonyl)vinyl]benzene (**3a**), in 89, 86, 85, and 32% yields, respectively (Table 1, entries 1–4). The ideal amount of *H*-phosphonate was then explored. When the reaction was carried out in the absence of diethyl *H*-phosphonate, the product was not obtained (Table 1, Entry 5). Addition of 0.5 equiv. of diethyl *H*-phosphonate resulted in a yield of 38% (Table 1, Entry 6). Increasing the amount of diethyl *H*-phosphonate to 1.1 equiv. (Table 1, Entry 1) gave a yield of 89%. Subsequently, the influence of a variety of catalysts on the model reaction was investigated (Table 1, Entries 1 and 7–10). Among the catalysts employed (i.e., $CuSO_4·5H_2O$, CuBr, CuI, $Cu(OAc)_2·H_2O$ and $NiCl_2·6H_2O$), $CuSO_4·5H_2O$ (Table 1, Entry 1) turned out to be the best, giving a yield of 89%. The influence of the amount of $CuSO_4·5H_2O$ was investigated. It was found that the yield increased from 24 to 89% with the increase of the catalyst from 10 to 25 mol-%, but the yield decreased when the amount was above 25 mol-% (Table 1, Entries 1, 11–13). The subsequent investigation of the influence of temperature (Table 1, Entries 1 and 14–16) revealed that the reaction proceeded most efficiently at 120 °C (Table 1, Entry 1). It can be seen that the yield increased over the temperature range of 80 to 120 °C, from 42 to 89%, and then gradually decreased to 85% after 140 °C was reached (Table 1, Entries 1 and 14–16). The effects of the acid used were also investigated (Table 1, Entries 1 and 17–19). A higher yield of **3a** (89%) was obtained when TFA was used (Table 1, Entry 1). Other acids resulted in relatively low yields of **3a**: i.e., AcOH (52%), $(CH_3)_3CCOOH$ (69%), TsOH (0%) (Table 1, Entries 17–19). The choice of solvent also highly affected the reaction efficiency. Compared with DMSO, DMF, toluene, 1,4-dioxane, and $(CH_3CO)_2O$ resulted in only trace amounts of the product (Table 1, Entries 20–23). The optimal amount of TFA was finally investigated (Table 1, Entries 1 and 24–25), which indicated that 0.2 equiv. of TFA

Table 2. Scope of the hydrosulfonylation.[a]



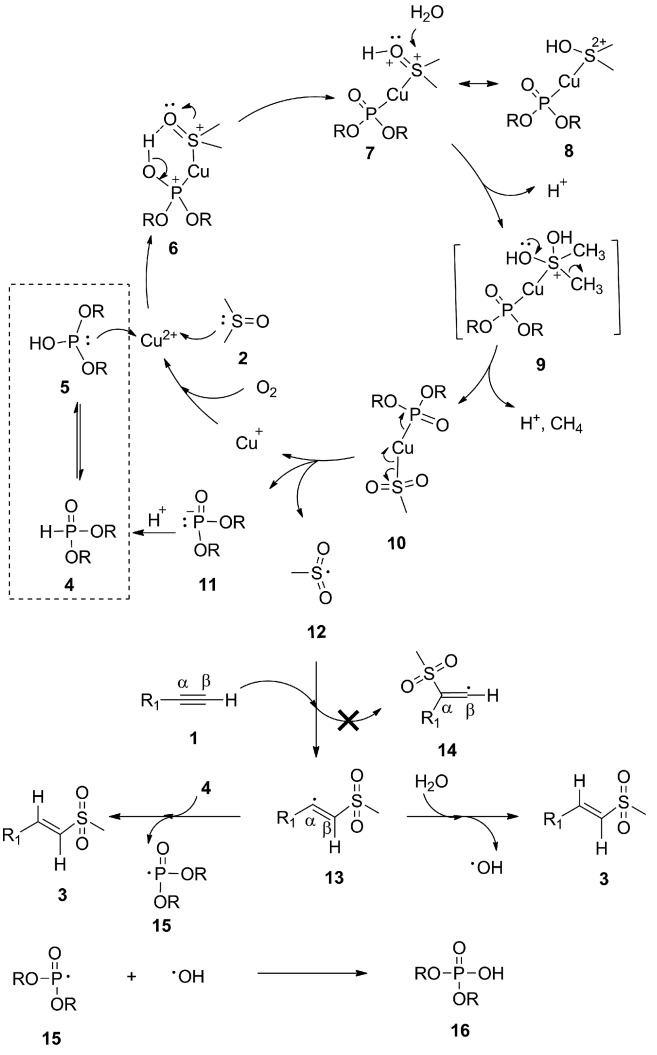
[a] Reaction conditions: **1** (1.0 mmol), **2** (2.0 mL), DEPH (1.1 mmol), $CuSO_4·5H_2O$ (25 mol-%), TFA (20 mol-%) at 120 °C for 10 h. [b] Isolated yields.

(Table 1, Entry 1) resulted in the most satisfactory yield. Further screening of the reaction time showed that 10 h was the best choice. Therefore, optimal reaction conditions involved 1.1 equiv. diethyl *H*-phosphonate, 25 mol-% $CuSO_4 \cdot 5H_2O$ and 20 mol-% TFA in DMSO at 120 °C for 10 h.

With the optimized conditions in hand, we next explored the scope of this hydrosulfonylation of various alkynes. As shown in Table 2, a large variety of aryl terminal alkynes, with both electron-donating (OCH_3, CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}) and electron-withdrawing groups (F, Cl, Br) on the aryl ring, reacted smoothly with **2**, affording the corresponding vinyl alkylsulfones **3a**–**3r** in good to excellent yields from 55 to 89%. The substituents on the benzene ring had no obvious influence on the corresponding yields. Functionalities such as halogen, methoxy, acetamide and cyano groups were well tolerated in the reaction processes. In addition, the reaction of 1-ethynylcyclohexene with DMSO efficiently afforded the conjugated sulfone **3s** in 82% yield. Most importantly, heteroaromatic alkynes also gave the corresponding products **3t**–**3w** in good to excellent yields from 60 to 75%. To our delight, the reaction of 1-phenylpropyne, an internal alkyne, with **2** afforded the vinyl sulfone **3x** in a satisfactory yield (68%). All products obtained (**3a**–**3x**) had an *E* configuration, which indicated a high stereoselectivity of this hydrosulfonylation reaction (spectra and characterization data can be found in the Supporting Information).

A plausible mechanism for the hydrosulfonylation reaction is depicted in Scheme 2. It is worth mentioning here that the dialkyl *H*-phosphonates occupy a major position in organophosphorus chemistry, since they are frequent intermediates in the synthesis of a variety of bioactive phosphorus-containing products.[18] A property that is most important from the point of view of the synthetic applications is the tautomeric equilibrium between their phosphite and phosphonate forms: the tricoordinate phosphorus form and the tetracoordinate phosphorus form.[19] Here, the cheap, easily prepared and preserved diethyl *H*-phosphonate **4** (tetracoordinate form) existed with its tautomer diethyl phosphite **5** (tricoordinate form). Initially, diethyl phosphite **5** and DMSO **2** coordinated with Cu^{2+} to form the copper complex **6** with concomitant formation of an intramolecular hydrogen bond (O–H···O=S) to give a six-membered ring. Subsequently proton transfer from the OH group to the oxygen atom of the S=O group occurred, leading to the formation of complex **7**. It is worth emphasizing here that complex **7** could be in resonance with **8**. The two positive charges at the sulfur atom of resonance structure **8** implied a great sensitivity of the protonated sulfinyl group to nucleophilic attack. A molecule of water can subsequently attack the protonated sulfinyl group of **7**, to give pentavalent intermediate **9**. Then intermediate **9** immediately loses a molecule of methane as well as a proton, to give copper complex **10**.

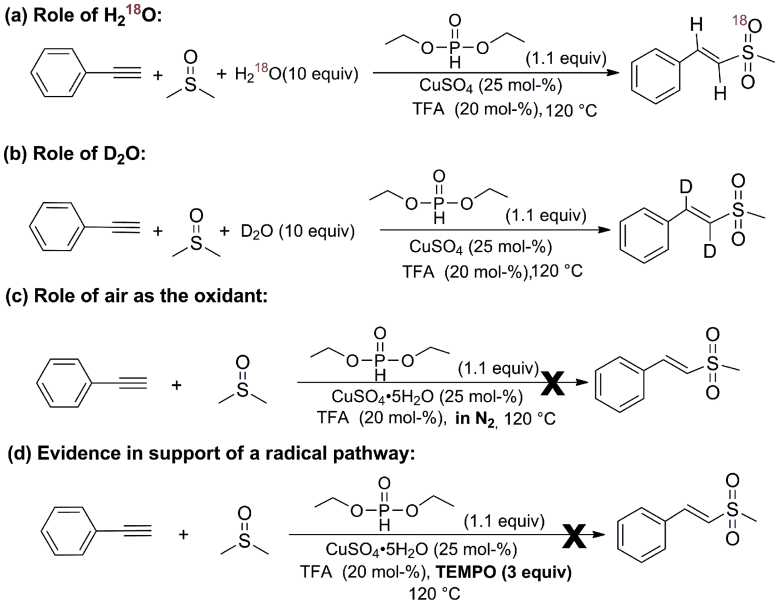
Copper complex **10** then homolytically cleaved to a phosphonate anion **11**, Cu^+ and sulfonyl radical **12**. Cu^+ was oxidized back to Cu^{2+} by oxygen in air, and phosphonate



Scheme 2. Plausible mechanism.

ion **11** was protonated to give diethyl *H*-phosphonate **4**. Here, the selective addition of radical **12** to the β position rather than α position of terminal alkyne **1**, afterwards, led to the formation of the more stable α-carbon-centered vinyl radical **13** rather than less stable β-carbon-centered vinyl radical **14**. The selective addition of **12** to **1** well explains the high regioselectivity of the hydrosulfonylation reaction. Then vinyl radical **13** interacted with water to yield the final vinyl sulfone **3** and hydroxy radical.[20] Meanwhile the vinyl radical **13** could react with another molecule of **4** to produce the final product **3** together with phosphite radical **15**. Then dialkyl phosphate **16** might possibly be formed by a termination reaction of phosphite radical **15** and hydroxy radical in the related reaction process.

More synthetic experiments were subsequently carried out to give support to the reaction mechanism mentioned above (Scheme 3). Isotopic labeling experiments with $H_2{}^{18}O$ and D_2O were then performed. The reaction of phenylacetylene with DMSO in the presence of 10 equiv. $H_2{}^{18}O$ afforded ^{18}O-labeled **3a** (Scheme 3-a), demonstrating clearly that the additional oxygen atom of **3a** originated from H_2O



Scheme 3. Proposed reaction of alkynes and DMSO with different reaction conditions. Reaction conditions: (a) **1a** (1.0 mmol), **2** (2.0 mL), DEPH (1.1 mmol), $CuSO_4$ (25 mol-%), TFA (20 mol-%), $H_2{}^{18}O$ (10 equiv.) at 120 °C for 10 h; (b) **1a** (1.0 mmol), **2** (2.0 mL), DEPH (1.1 mmol), $CuSO_4$ (25 mol-%), TFA (20 mol-%), D_2O (10 equiv.) at 120 °C for 10 h; (c) **1a** (1.0 mmol), **2** (2.0 mL), DEPH (1.1 mmol), $CuSO_4·5H_2O$ (25 mol-%), TFA (20 mol-%) at 120 °C under nitrogen atmosphere for 10 h; (d) **1a** (1.0 mmol), **2** (2.0 mL), DEPH (1.1 mmol), $CuSO_4·5H_2O$ (25 mol-%), TFA (20 mol-%), TEMPO (3 equiv.) at 120 °C for 10 h.

instead of O_2 in the air. The reaction was also carried out in the presence of 10 equiv. D_2O, and D-labeled **3a** was obtained in this case (Scheme 3-b). As illustrated in the mechanism, it is O_2 from the air that oxidizes Cu^+ back to Cu^{2+}. The reaction in the absence of oxygen was therefore carried out. When the reaction was carried out under a nitrogen atmosphere, the corresponding vinyl sulfone **3a** was not obtained (Scheme 3-c). This result showed that the copper-catalyzed hydrosulfonylation of alkynes required the presence of oxygen. A radical pathway was also thought to be involved in this reaction. The following radical-trapping experiments might support this assumption. When TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), a well-known radical-capturing species, was added to the reaction system, the reaction was completely suppressed (Scheme 3-c) (for details see the Supporting information).

Conclusions

A novel and practical $CuSO_4·5H_2O$-*H*-phosphonate-catalyzed synthesis of (*E*)-vinyl alkylsulfones from alkynes and widely available DMSO was developed. The cleavage of the C–S bond of DMSO catalyzed by $CuSO_4·5H_2O$-*H*-phosphonate was the key step for this transformation. The method described in this paper may possess some advantages of cheap catalysts, readily available starting materials, operational simplicity and high stereo- and regioselectivity, opening a new door to the construction of vinyl sulfones. Studies of the detailed mechanism of this process and its application are currently underway in our laboratory.

Experimental Section

Experimental Procedures for the Synthesis of Vinyl Alkylsulfones (3a–3x): A 25-mL round-bottom flask containing a stirrer bar was charged with a terminal alkyne (1.0 mmol), DMSO (2.0 mL), DEPH (1.1 mmol), $CuSO_4·5H_2O$ (25 mol-%), and TFA (20 mol-%). The reaction was stirred at 120 °C for 10 h (monitored by TLC). Upon completion of the reaction, the mixture was diluted with brine (3.0 mL) and extracted with dichloromethane (10 mL × 3). The organic layers were combined, washed with brine, dried with anhydrous Na_2SO_4, and filtered. The solvents were removed by rotary evaporator under reduced pressure and the residue was purified by flash chromatography (silica gel, gradient eluent of petroleum ether/ethyl acetate = 2:1) to yield the desired product.

Acknowledgments

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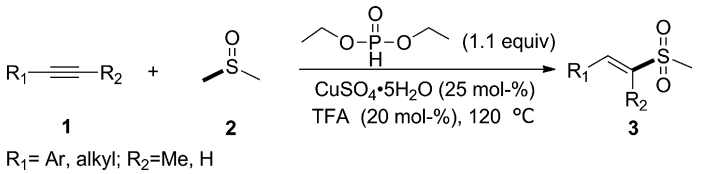

A novel and efficient $CuSO_4 \cdot 5H_2O$-*H*-phosphonate-catalyzed synthesis of (*E*)-vinyl alkylsulfones from alkynes and widely available DMSO was developed.

Keywords: Copper / Phosphonates / C–S Bond Formation / Synthetic methods / Vinyl sulfones

