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Temperature-dependent synthesis of vinyl sulfones and β-hydroxy sulfones from *t*-butylsulfinamide and alkenes under aerobic conditions†

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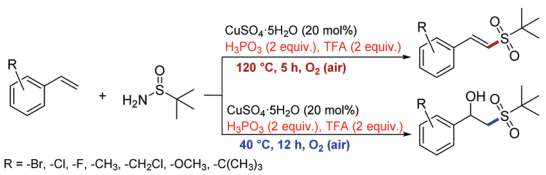
A novel temperature-dependent synthesis of organic sulfones from *t*-butylsulfinamide and alkenes under aerobic $CuSO_4$-phosphorous acid catalyzed conditions was developed. *Via* this newly developed method, a series of vinyl sulfones and β-hydroxy sulfones were synthesized at 120 °C and 40 °C, respectively.

Sulfone-containing molecules, such as vinyl sulfones and β-hydroxysulfones, are pharmaceutically significant compounds,[1] which exhibit a wide range of biological activities including protease inhibition,[2] anticancer,[3] anti-HIV[4], anti-Parkinson's disease[5], *etc.* Besides, they are also widely used as synthetic building blocks for numerous transformations.[6] Traditional synthetic methods for the synthesis of vinyl sulfones[7–9] and β-hydroxy sulfones[10,11] suffer from obvious limitations such as unavailable starting materials, harsh reaction conditions, poor selectivity, requirement of noble transition-metal catalysts, *etc.* During the last decade, the construction of C–S bonds through radical-initiated cross-coupling reactions[12] of alkenes/alkynes and their derivatives with commonly used sulfonyl chlorides,[13] sulfonyl hydrazides,[14] sodium sulfinates[15] and sulfinic acids[16] has been well explored and continuously reported. Besides, uncommonly used sulfur sources, such as thiols/thiophenols,[17] disulfides,[18] DMSO,[19] tosylmethyl isocyanide (TosMIC)[20] and DABCO·$(SO_2)_2$,[21] were also frequently employed for the synthesis of organic sulfones. Even though these strategies greatly enrich the diversity of the construction of C–S bonds and contribute significantly to the synthetic methodology of organic chemistry, the pursuit of novel strategies for the synthesis of sulfone-containing molecules is still tireless.[22]

t-Butylsulfinamide, known as a chiral source due to its low cost and easy preparation properties, has been widely used to synthesize various chiral amines and chiral ligands in metal-catalyzed asymmetric reactions.[23] In our previously reported studies related to the construction of C–S bonds,[24] we disclosed an efficient method for the synthesis of organic sulfones through $CuSO_4$-phosphorous acid catalyzed N–S bond cleavage of *t*-butylsulfinamide.[24a] It is worth mentioning here that *t*-butylsulfinamide was used as a sulfur source for the first time concerning the construction of C–S bonds. Encouraged by this interesting transformation, we continuously committed our efforts to exploring the diverse reactivity of *t*-butylsulfinamide in the challenging C–S bond construction. Herein, we would like to disclose a temperature-dependent synthesis of vinyl sulfones and β-hydroxy sulfones from *t*-butylsulfinamide and alkenes under aerobic $CuSO_4$-phosphorous acid catalyzed conditions (Scheme 1). This newly developed synthetic method broadens the reaction scope of *t*-butylsulfinamide and provides an alternative for the synthesis of pharmaceutically and biologically important vinyl sulfones and β-hydroxy sulfones.

Initially, the optimization reaction conditions for the sulfonylation of alkenes were investigated using styrene **1a** and *t*-butylsulfinamide **2** as model substrates (Table 1). We were glad to observe that styrene **1a** was successfully converted in the presence of 20 mol% of $CuSO_4·5H_2O$, 2 equiv. of H_3PO_3 and 2 equiv. of trifluoroacetic acid (TFA) at 80 °C for 5 h under



Scheme 1 Strategies for the synthesis of vinyl sulfones and β-hydroxy sulfones.

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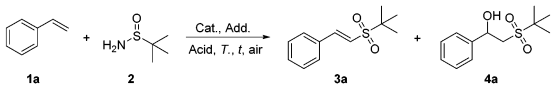
Table 1 Optimization of the reaction conditions[a]

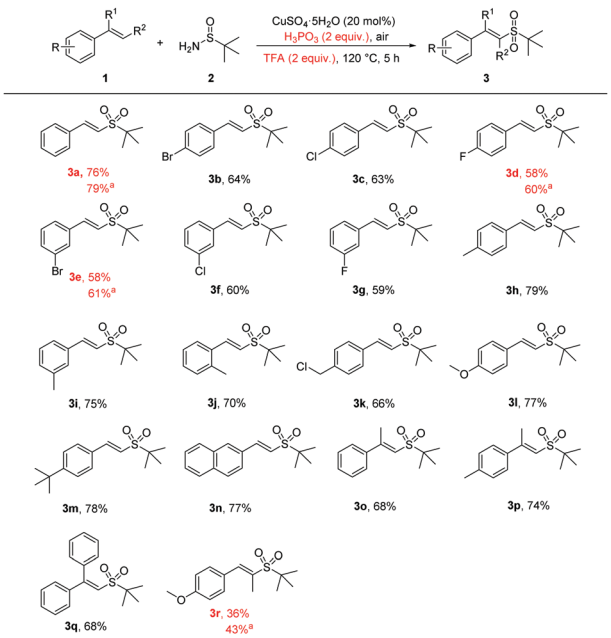


Entry	Cat. (mol%)	Add. (equiv.)	Acid (equiv.)	T (°C)	t (h)	**3a**/**4a**[b]	Yield (%)
1	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	80	5	3/1	53[c]
2	CuI (20)	H_3PO_3 (2)	TFA (2)	80	5	4/1	21[c]
3	CuBr (20)	H_3PO_3 (2)	TFA (2)	80	5	4/1	20[c]
4	$Cu(OAc)_2$ (20)	H_3PO_3 (2)	TFA (2)	80	5	3/1	24[c]
5	$CuSO_4$ (20)	H_3PO_3 (2)	TFA (2)	80	5	2/1	30[c]
6	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	H_2SO_4 (2)	80	5	4/1	37[c]
7	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TMA (2)	80	5	ND	NR
8	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	AcOH (2)	80	5	ND	NR
9	$CuSO_4·5H_2O$ (20)	DMPH (2)	TFA (2)	80	5	2/1	38[c]
10	$CuSO_4·5H_2O$ (20)	DEPH (2)	TFA (2)	80	5	4/1	32[c]
11	$CuSO_4·5H_2O$ (20)	DIPPH (2)	TFA (2)	80	5	3/1	33[c]
12	$CuSO_4·5H_2O$ (20)	DPPH (2)	TFA (2)	80	5	3/1	29[c]
13	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	100	5	5/1	61[c]
14	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	120	5	20/1	76[c]
15	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	140	5	10/1	75[c]
16	$CuSO_4·5H_2O$ (20)	H_3PO (2)	TFA (2)	60	5	1/5	39[d]
17	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	40	5	1/10	35[d]
18	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	RT	5	1/10	32[d]
19	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	40	9	1/20	48[d]
20	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	40	12	1/30	69[d]
21	$CuSO_4·5H_2O$ (20)	H_3PO_3 (2)	TFA (2)	40	15	1/50	68[d]

[a] Reaction conditions: **1a** (1.0 mmol), **2** (1.2 mmol), Cat. (20 mol%), Add. (2 equiv.) and acid (2 equiv.) were mixed and stirred at RT-140 °C for 5–15 h under open-air conditions. [b] The mol-ratio of **3a**/**4a** was detected by diagnostic peak integration in ^{1}H-NMR of the crude reaction mixture. [c] Isolated yields for **3a**. [d] Isolated yields for **4a**. TMA = trimethylacetic acid. ND = not detected. NR = no reaction. DMPH = dimethyl *H*-phosphonate. DEPH = diethyl H-phosphonate. DPPH = diphenyl H-phosphonate. DIPPH = diisopropyl *H*-phosphonate. RT = room temperature.

open-air conditions. However, two sulfonylated compounds, (*E*)-vinyl sulfones and β-hydroxy sulfones (**3a** and **4a**), were found in the crude reaction mixture with a mol-ratio of 3/1 and an isolated yield of 53% of **3a** was obtained (entry 1). In order to improve the mol-ratio and isolated yield of **3a**, the catalyst, acid and additive employed in this transformation were carefully screened. However, as can be seen in entries 2–5, 20 mol% of CuI, CuBr, $Cu(OAc)_2$ and $CuSO_4$ could catalyze the reaction, but the efficiency (21–30%) was not better than that of $CuSO_4·5H_2O$ (53%). The use of other acids, such as H_2SO_4, trimethylacetic acid (TMA) and AcOH, as well as other additive *H*-phosphonate esters, such as dimethyl *H*-phosphonate (DMPH), diethyl *H*-phosphonate (DEPH), diisopropyl *H*-phosphonate (DIPPH) and diphenyl *H*-phosphonate (DPPH), all failed to provide a satisfactory isolated yield of **3a** (entries 6–12). Surprisingly, when the reaction temperature increased from 80 °C to 120 °C, the mol-ratio of **3a**/**4a** and isolated yield of **3a** were all significantly increased (entries 1, 13 and 14). However, when a higher temperature (140 °C) was used, the isolated yield of **3a** was slightly decreased in spite of a higher mol-ratio of **3a**/**4a** (entry 15). Therefore, the optimal reaction condition for the synthesis of **3a** was 120 °C. On the contrary, when the reaction mixture was stirred at low temperatures for 5 h, the mol-ratio of **3a**/**4a** decreased and the isolated yield of the main product **4a** ranged from 32–39% (entries 16–18). In order to get a satisfactory isolated yield of **4a**, the reaction was carried out at 40 °C for prolonged reaction times (9–15 h). As can be seen in entries 19–21, at least 12 h was necessary for the synthesis of compound **4a**.

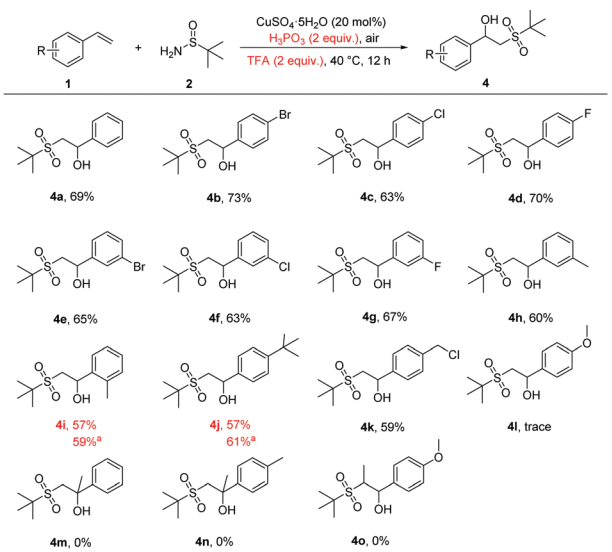
Then, the substrate scope of alkenes and *t*-butylsulfinamide under the optimized reaction conditions was explored. As demonstrated in Scheme 2, various aromatic alkenes were smoothly



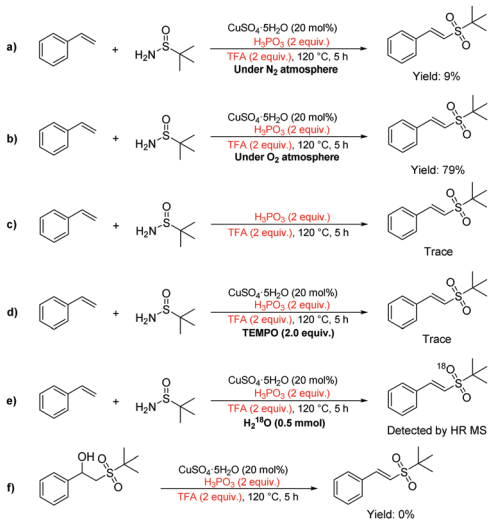
Scheme 2 Scope of vinyl sulfones. Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), H_3PO_3 (2 equiv.), $CuSO_4·5H_2O$ (20 mol%), and TFA (2 equiv.) were mixed and stirred at 120 °C for 5 h. Isolated yields were provided. [a] Under O_2 atmosphere.

converted to the corresponding (*E*)-vinyl sulfone derivatives *via* direct sulfonylation with *t*-butylsulfinamide at 120 °C under aerobic conditions. Both electron-withdrawing groups (–Br, –Cl, or –F) and electron-donating groups (–CH_3, –CH_2Cl, –OCH_3, or –$C(CH_3)_3$) on the phenyl ring of the aromatic alkenes were suitable for this protocol, and the corresponding (*E*)-vinyl sulfones were obtained in moderate to good yields (**3b–m**). Aromatic alkenes with electron-donating groups (**3h–m**) gave slightly higher yields than those with electron-withdrawing groups (**3b–g**). In addition, polycyclic aromatic alkenes, 2-vinylnaphthalene, could also be converted in this reaction to afford (*E*)-2-(2-(*t*-butylsulfonyl)vinyl)naphthalene in a yield of 77% (**3n**). Furthermore, several disubstituted alkenes, including prop-1-en-2-ylbenzene, 1-methyl-4-(prop-1-en-2-yl)benzene, ethene-1,1-diyldibenzene and (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene, were employed to react with *t*-butylsulfinamide in this reaction. As can be seen, the 1,1-disubstituted terminal alkenes were successfully converted to the corresponding vinyl sulfones with relatively high yields (**3o–q**, 68–74%). Meanwhile, the 1,2-disubstituted non-terminal alkene was converted with relatively low yields (**3r**, 36%).

Furthermore, the synthesis of β-hydroxy sulfones was also carried out at 40 °C for 12 h under open-air conditions as shown in Scheme 3. Aromatic alkenes with both electron-withdrawing groups (–Br, –Cl, or –F) and electron-donating groups (–CH_3, –CH_2Cl, or –$C(CH_3)_3$) were smoothly converted to the corresponding β-hydroxy sulfone derivatives with moderate to good yield (**4b–k**, 57–73%). Contrary to the synthesis of vinyl sulfones, aromatic alkenes with electron-withdrawing groups (**4b–g**) gave slightly higher yields than those with electron-donating groups (**4h–k**). Aromatic alkenes with strong electron-donating groups (–OCH_3) as well as disubstituted alkenes failed to be converted to the corresponding β-hydroxy sulfone (**4l–o**).



Scheme 3 Scope of β-hydroxy sulfones. Reaction conditions: **1** (1.0 mmol), **2** (1.2 mmol), H_3PO_3 (2 equiv.), $CuSO_4·5H_2O$ (20 mol%), and TFA (2 equiv.) were mixed and stirred at 40 °C for 12 h. Isolated yields were provided. [a]Under O_2 atmosphere.

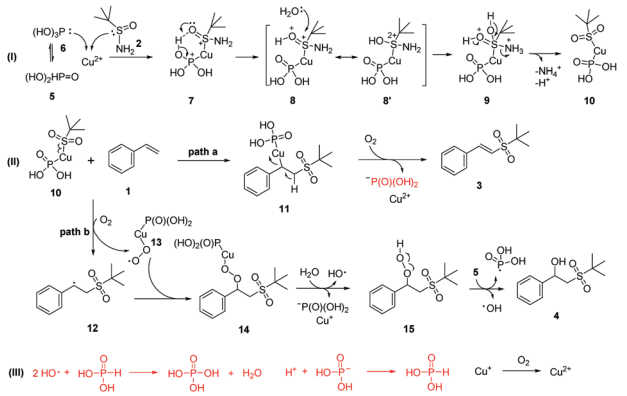


Scheme 4 Control experiments.

To gain further insight into the reaction mechanism, a series of control experiments were performed as shown in Scheme 4.

Firstly, when the reaction was carried out at 120 °C under a N_2 atmosphere, only 9% of the corresponding vinyl sulfone was obtained (Scheme 4a), which indicated that the oxygen was necessary in this transformation. However, when the reaction was performed under O_2 atmosphere, the corresponding vinyl sulfone was obtained with a yield of 79% (Scheme 4b), which was only slightly higher than that under open-air conditions (76%). When the reaction was carried out in the absence of $CuSO_4·5H_2O$ or in the presence of 2.0 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), only a trace of **4a** was found (Scheme 4c and d), indicating that a Cu(II)-promoted radical pathway was possibly involved in this reaction process. An isotopic labelling experiment clearly demonstrated that the additional oxygen atom of the sulfone groups in **3a** and **4a** originated from H_2O instead of O_2 in the air (Scheme 4e). Finally, an intermolecular transformation from β-hydroxy sulfone **4a** to vinyl sulfone **3a** was performed at 120 °C for 5 h (Scheme 4f). However, no corresponding vinyl sulfone was obtained, which suggested that vinyl sulfones were not synthesized *via* the simple dehydration of β-hydroxy sulfones under high temperatures.

Referring to the literature[14c] and our previous work,[24a] a plausible mechanism for the reaction is proposed in Scheme 5. Initially, the tricoordinated phosphorous acid **6** and *t*-butylsulfinamide **2** coordinate with Cu^{2+} to form complex **7**. In this case, a six-membered ring is generated inside **7** as a result of the formation of an intramolecular hydrogen bond (O–H···O=S). Subsequently, a proton transfers from the OH group of **6** to the oxygen of the S=O group, giving the copper complex **8**, which can resonate with **8′**. The two positively charged sulfur atoms in **8′** imply the highly electrophilic ability of the protonated sulfonyl group. Meanwhile, one molecule of water attacks the protonated sulfonyl group of **8**, affording the pentavalent intermediate **9**. Then, intermediate **9** loses an ammonium and a proton, yielding the key intermediate copper complex **10** (Scheme 5I). When the



Scheme 5 Plausible mechanism.

reaction is performed at high temperatures, the copper complex **10** undergoes homolytic cleavage and adds to alkene **1** *via* 1,2-addition, affording the corresponding complex **11** (Scheme 5II, path a). Complex **11** undergoes a dehydrative β-elimination to afford the vinyl sulfone **3**. The residual copper–phosphorous complex is oxidized to recycle catalyst Cu^{2+} and non-toxic phosphite anions. When the reaction is performed at low temperatures, complex **10** undergoes homolytic cleavage to form a *t*-butyl sulfonyl radical, which reacts with alkene **1** to afford the radical **12**. Meanwhile, the residual copper-phosphorous radical captures one molecule of O_2, resulting in an active-oxygen complex **13**.[21a] Then, the radical **12** is attacked by this active-oxygen complex **13**, affording complex **14**. Complex **14** reacts with water, forming hydroperoxide **15**, phosphite anions and copper(I) ions. The oxygen–oxygen bond of the hydroperoxide of **15** is weak and undergoes homolysis to react with another molecule **5** to yield β-hydroxy sulfone **4** and a hydroxyl radical (Scheme 5II, path b). Finally, the hydroxyl radical is quenched by phosphorous acid to give phosphoric acid, the phosphite anion was protonated by TFA to form phosphorous acid and Cu^{+} is oxidized back to Cu^{2+} by O_2 in the air (Scheme 5III).

Conclusions

In conclusion, we developed a novel temperature-dependent methodology for the synthesis of organic sulfones using *t*-butylsulfinamide as a sulfur source under aerobic $CuSO_4$-phosphorous acid catalyzed reaction conditions. Two different kinds of organic sulfones, vinyl sulfones and β-hydroxy sulfones were synthesized through the cleavage of the N–S bond of *t*-butylsulfinamide and the formation of C–S bonds with alkenes at 120 °C and 40 °C, respectively. The newly developed synthetic method broadens the reaction scope of *t*-butylsulfinamide and provides an alternative for the synthesis of pharmaceutically and biologically important vinyl sulfones and β-hydroxy sulfones.

Conflicts of interest

There are no conflicts to declare.

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