CuI/L-proline potassium salt catalysed synthesis of vinyl sulfones via coupling reaction of vinyl bromides with sulfinic acid salts in ionic liquid

Weiliang Bao* and Congna Wang

Department of Chemistry, Zhejiang University, Xi Xi Campus, Hangzhou, Zhejiang 310028, China

Catalysed by CuI/L-proline potassium salt, which serves as both base and ligand, the coupling reaction of vinyl bromides with sulfinic acid salts occurs at 110 °C in ionic liquid to give the corresponding vinyl sulfones in good yields.

Keywords: CuI/L-proline potassium salt, vinyl sulfones, vinyl bromides

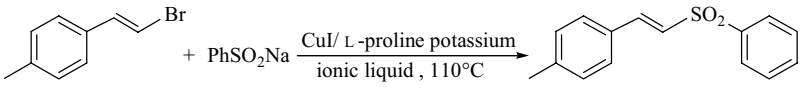
In recent years, the applications of Cu(I) as a transition metal catalyst have been attracting much attention.[1] Compared with other metal catalysts such as Rh, Pd, Cu is the most economical and available one. What's more, it has its own good catalytic effect in some types of organic reactions. For instance: Li reported using CuI/Dabco as the catalytic system for the Heck–type reaction;[2] Tang synthesised indoles via Friedel–Crafts reaction catalysed by $Cu(OTf)_2$;[3] our group used CuI as catalyst for Ullmann-type reaction;[4] and Ma reported the synthesis of aryl sulfones via CuI-catalysed coupling reaction of aryl halides with sulfinic acid salts.[5]

In view of the importance of vinyl sulfones as versatile intermediates in organic synthesis, there are many research results dealing with their synthetic methods, such as Knoevenagel condensation of aromatic aldehydes with sulfonylacetic acids;[6] Horner–Emmons reaction of carbonyl compounds and sulfonyl phosphones;[7] β-elimination of selenosulfones and halosulfones.[8] So we think it's a significative challenge using L-proline-promoted CuI as catalytic system to develop a new way to synthesise vinyl sulfones.

The coupling of β-bromo-4-methylstyrene with sodium benzenesulfinate was chosen as a model to explore the optimum reaction condition, and the results were illustrated in Table 1. No obvious distinction was observed whenever using CuI or CuBr as the catalyst, but the reaction temperature is found to be the most important factor. The coupling was very slowly at 80 °C and only a little product was formed even after 10 h (Table 1, entries 1 and 2). When the temperature was raised to 110 °C, the yield increased if the reaction time was maintained for 10 h (Table 1, entries 3 and 4). Above 110 °C there was no increase in yield (Table 1, entries 14 and 15). Under the same reaction condition, higher yield was not obtained by extending the reaction time (Table 1, entries 13 and 15). But the yield was greatly affected by the amount of catalyst. When using 30 %CuI as catalyst compared with 10 %CuI, the yield increased evidently, but the uptrend of yield decreased when the amount of CuI increased to 40 % (Table 1, entries 8 and 10). From the economical consideration, using 30 %CuI in this experiment is the best choice. In this reaction, no differences in yields were found whenever using the organic solvent or ionic liquid. As the ionic liquid can be recycled, so we finally chose the ionic liquid as the solvent. We also try to examine whether the yield will change in the different ionic liquids, in fact, there is almost no change.

From the results above, we could conclude that using 30 %CuI/L-proline potassium salt as the most productive catalytic dose and $[bmim]BF_4$ as the solvent at 110 °C in 10 h is the optimum condition for this coupling reaction. Its applicative range was then explored with different vinyl bromides and sulfinic acid salts, and the results were summarised in Table 2. We found that both electron-rich and electron-deficient vinyl bromides proved to provide corresponding product in good yield (like entry 3 and entry 2). Compared with $PhSO_2Na$, CH_3SO_2Na as the sulfinic acid salt reacting with the same vinyl bromides, the reaction is much easier to occur, and the yield is higher.

Table 1 Reaction of β-bromo-4-methylstyrene with sodium benzenesulfinate

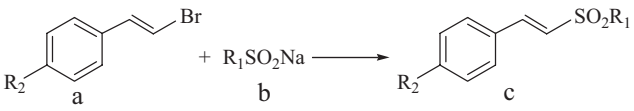


Entry	Reaction system	Yield[b]/%
1	10%CuI/L-proline potassium/80 °C/DMSO/10 h	10
2	10%CuI/L-proline potassium/80 °C/$[bmim]BF_4$/10 h	10
3	10%CuI/L-proline potassium/110 °C/DMSO/10 h	30
4	10%CuI/L-proline potassium/110 °C/$[bmim]BF_4$/10 h	32
5	10%CuI/L-proline potassium/110 °C/DMSO/7 h	23
6	10%CuI/L-proline potassium/110 °C/[bmim]Br/10 h	30
7	30%CuI/L-proline potassium/110 °C/DMSO/10 h	78
8	30%CuI/L-proline potassium/110 °C/$[bmim]BF_4$/10 h	80
9	40%CuI/L-proline potassium/110 °C/DMSO/10 h	79
10	40%CuI/L-proline potassium/110 °C/$[bmim]BF_4$/10 h	82
11	30%CuI/L-proline potassium/110 °C/[bmim]Br/10 h	80
12	30%CuBr/L-proline potassium/110 °C/$[bmim]BF_4$/10 h	78
13	30%CuI/L-proline potassium/100 °C/$[bmim]BF_4$/10 h	73
14	30%CuI/L-proline potassium/120 °C/$[bmim]BF_4$/10 h	77
15	30%CuI/L-proline potassium/110 °C/$[bmim]BF_4$/24 h	80

[a]Reaction conditions: L-proline potassium (0.6 mmol), CuI (0.3 mmol), β-bromo-4-methylstyrene (1.0 mol), $PhSO_2Na$ (1.2 mmol), $[bmim]BF_4$(2 ml), 110 °C, under N_2 atmosphere, 10 h. [b]Isolated yield.

* Correspondent. E-mail: wbao@hzcnc.com

Table 2 Transformation of vinyl bromides into vinyl sulfones by the using of L-proline–promoted CuI as the catalyst



Entry	R_1	R_2	M.p./°C	Lit. m.p./°C	Yield/%
1	CH_3	H	79	80[9]	83
2	CH_3	Cl	127	127–128[9]	80
3	CH_3	OCH_3	139	143–144[9]	81
4	CH_3	CH_3	111	109–110[10]	81
5	Ph	H	74	76[11]	67
6	Ph	Cl	130	131[11]	71
7	Ph	CH_3	138	139–140[12]	80
8	Ph	OCH_3	120	120–121[12]	63
9	Ph	Br	150	150–152[12]	63

Recycling ability is one of the important characters for the ionic liquid.[13] For every substrate, the ionic liquid can be reused for more than 3 times. The results are in Table 3. We found that the yields only had declined a little. Recycling the ionic liquid for the third time, the yield is still quite good. Once the reaction finished and the product was extracted, the ionic liquid can be reused after dryness.

In summary, we have reported a novel and efficient synthetic way of vinyl sulfones, which has an accessible large range of raw material choice and reaction conditions easy to control. The highly effective Cu(I) catalytic system, which allowed for coupling reaction of vinyl bromides with sulfinic acid salts formed vinyl sulfones in good yields.

Experimental

Typical procedure for the vinyl sulfones of vinyl bromides with sulfinic acid salts: a mixture of β-bromo-4-methylstyrene(1 mmol), sodium benzenesulfinate (1.2 mmol), copper iodide(0.3 mmol), L-proline potassium salt (0.6 mmol), and 2 ml of [bmim]BF_4 in a little bottle was heated to 110 °C under N_2 for 10 h. After the reaction is completed, the reaction mixture is extracted by 5 ml diethyl ether for 3 times. The corresponding product was separated by column chromatography in a good yield.

Table 3 Recycling of the ionic liquid with the reaction of the β-bromo-4-methylstyrene as the substrate

Recycled	Time/h	Yield/%
1	10	80
2	10	78
3	10	76

(E)-1-phenylsulfonyl-2-(4-tolyl)ethene **(7c):** M.p. 138 °C. IR(KBr): 1604, 1309, 1149 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.35 (s, 3H), 6.87(d, J = 15.4 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.52–7.61 (m, 3H), 7.66 (d, J = 15.4 Hz, 1H), 7.93 (d, J = 7.3 Hz, 2H). MS (*m/z*): 258(M^+, 25), 116(100).

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