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Sheng-Rong Guo [a] & Yan-Qin Yuan [a]
[a] Department of Chemistry , Lishui University , Lishui, China
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CuI/L-Proline-Catalyzed Synthesis of Vinyl Sulfides in 95% Alcohol

Sheng-Rong Guo and Yan-Qin Yuan
Department of Chemistry, Lishui University, Lishui, China

Abstract: A method for the synthesis of vinyl sulfides using the simple CuI/L-proline as a catalyst system is reported. The best yields were obtained in the 95% ethanol with 10 mol% CuI, 20 mol% L-proline, and 1.2 equiv of K_2CO_3. The amino acids act as base and excellent promoter for the copper-catalyzed coupling reactions, and this protocol tolerates both aromatic and heterocyclic thiols and avoids using other expensive additives.

Keywords: Cross-coupling reaction, L-proline, thiols, vinyl sulfide

Vinyl sulfides play an important role as synthetic intermediates in organic chemistry. They are equivalents of carbonyl compounds and can be transformed to sulfoxides and sulfones. Methods for the formation of vinyl–sulfur bonds are indispensable tools in synthetic chemistry. Their importance stems from the prevalence of vinyl sulfides in many molecules that are of biological, pharmaceutical, and materials interest.[1–5]

Because of the importance of these compounds, there have been a number of reported methods for synthesizing vinyl sulfides.[6,7] Among them, the addition of thiols to alkynes by free radical conditions or by anionic addition is one of the most straightforward methods of obtaining vinyl sulfides,[8,9] affording the anti-Markovnikov product, usually as a stereoisomeric mixture. The Wittig reaction has also been utilized in the synthesis of vinyl sulfides, but this method requires the use of strong bases, and the synthesis of the appropriate Wittig reagents can be problematic.[10,11] The cross-coupling reaction of vinyl halides with metal thioalkoxides in the presence of a transition-metal catalyst,[12–14] as well

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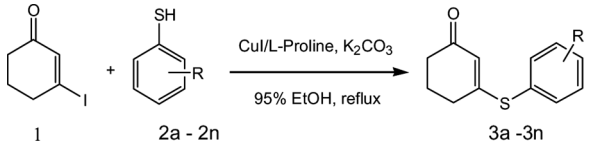
Address correspondence to Guo Sheng-rong, Department of Chemistry, Lishui University, Lishui, China. E-mail: guosr9608@163.com



Scheme 1.

as the reaction of vinyl halides with sodium and lithium thiols or their tin analogs cross-coupling on organic halides in the presence of the catalyst $Cu(phen)(PPh_3)_2NO_3$,[15] is also one of the most valuable protocols to gain the vinyl sulfides. However, the scope and functional group tolerance of these cross-coupling reactions have not been fully explored.

Recently there has been a resurgence in interest in developing L-proline-catalyzed cross-coupling reactions. The amino acid proline is a remarkable molecule that has become important in cross-coupling reaction catalysis.[16–19] Ma and Cai[17] recently reported that CuI/L-proline (or N-methylglycine) is an efficient catalytic system to make Ullmann-type arylamination work at mild conditions, and Zheng et al.[20] reported that the CuI/L-proline system in ionic liquid can promote the cross-coupling reaction of vinyl bromides and thiols with K_2CO_3 as the base at 110°C, but they used expensive ionic liquids as solvents. These copper-based methods work extremely well with soft nucleophiles such as amino, sulfur, selenium, and phosphorus. Because of the importance of vinyl sulfides and the lack of a general protocol for their synthesis, we now report a general method for the cross-coupling of vinyl iodides and thiols, using CuI/L-proline as the catalyst, K_2CO_3 as the base, and 95% alcohol as solvent to synthesize vinyl sulfides (Scheme 1).

The optimization process was performed using the cross-coupling of 4-fluorothiophenol and 3-iodo-cyclohexenone. We first explored the coupling reaction catalyzed by 10 mol% CuI and 20 mol% L-proline in alcohol at reflux in the presence of K_2CO_3. The reaction proceeded well, and the vinyl sulfide was obtained in good yield. Then we scanned the effects of bases, using 10 mol% CuI and 10 mol% L-proline as catalyst. Bases such as K_2CO_3, K_3PO_4, and Cs_2CO_3 were very effective. Other bases such as Et_3N, pyridine, piperidine, and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were less effective (Table 1). We also observed the impact of solvents and found that the DMF, DMSO, glycol, and ionic liquid $[Bmim]BF_4$ were also good solvents for the coupling reaction, but the best yield and the simplest method to separate the product used 95% alcohol.

Thus, the optimized reaction conditions utilized 10 mol% CuI, 20 mol% L-proline, and 1.2 equiv of K_2CO_3 in 10 ml of 95% EtOH at

Table 1. Effects of bases and solvents on the coupling of 4-flurothiophenol and 3-iodo-cyclohexenone catalyzed by 10 mol% CuI and 20 mol% L-proline[a]

Entry	Base	Solvent	Yield[b] (%)
1	K_2CO_3	95% EtOH	92
2	K_2CO_3	DMF	86
3	K_2CO_3	DMSO	83
4	K_2CO_3	glycol	84
5	K_2CO_3	[Bmim]BF_4	85
6	Cs_2CO_3	95% EtOH	93
7	K_3PO_4	95% EtOH	86
8	Et_3N	95% EtOH	54
9	DBU	95% EtOH	28
10	Pyridine	95% EtOH	35
11	Piperidine	95% EtOH	42

[a]Reaction conditions: 10 mol% CuI, 20 mol% L-proline, and 1.2 equiv of K_2CO_3 in 5–10 ml above solvent at 80°C under N_2 atmosphere.
[b]Isolated yields after reaction 8 h.

reflux under an N_2 atmosphere. In the first part of this study, these reaction conditions were applied to the coupling of various functionalized thiophenol and 3-iodo-cyclohexenone (Table 2).

As can be seen, both electron-rich aromatic (or electron-poor) and heterocyclic thiols can be coupled to 3-iodo-cyclohexenone in good yields; however, in contrast to the coupling of aryl and alkanethiols, the coupling reactions were slower. The thiohydroxyl is more active than the hydroxyl. The structure of product **3f** proved to be the sulfide by comparing the ^{1}H NMR spectra of **3f** with the raw material 2-ethyl-4-mercaptophenol; the aryl thiols containing -OH (compound **3f**) were efficiently converted to the product (Scheme 2), but of the aryl thiols containing $-NH_2$ (compound **3m**) only 40% were converted to the product.

A second part of this work involved the application of different amino acids as the catalyst. Amino acids can act both as acid and base and can also facilitate chemical transformations in concert, similar to enzymatic catalysis. Another virtue of amino acids is the excellent ability to complex to Cu(I) salt. In this reaction, we also used the L-proline as an additive. Some other amino acids or other additives were also screened and proven effective, but best yield was obtained when L-proline was the additive. If no amino acid was added, the reaction time and yield were not perfect (Table 3).

In conclusion, we have developed a CuI- and L-proline-catalyzed system for the synthesis of vinyl sulfides in good yields using a combination of 10 mol% CuI and 20 mol% L-proline in 95% ethanol. This method

Table 2. Coupling reaction of 3-iodo-cyclohexenone with various aryl thiols catalyzed by CuI/L-proline system[a]

Product	ArSH	Time (h)	Yield[b] (%)
3a	4-Flurothiophenol	6	92
3b	3-Flurothiophenol	6	90
3c	2-Flurothiophenol	6	88
3d	3,5-Diflurothiophenol	8	84
3e	4-Trifluoromethoxythiophenol	8	80
3f[c]	2-Ethyl-4-mercapto-phenol	4	82
3g	(4-Bromo-phenyl)-methanethiol	8	85
3h	2-Isopropylthiophenol	4	91
3i	2,6-Dimethylthiophenol	4	88
3j	2-Ethoxythiophenol	4	92
3k	2,6-Bistrifluoromethylthiophenol	9	78
3l	3-Ethylthiophenol	6	82
3m[c]	4-Amino-2-fluoro-thiophenol	6	40
3n	Thiazole-2-thiol	12	85
3o	Pyrimidine-2-thiol	12	87

[a]Reaction conditions: 3-iodo-cyclohexenone (2.0 mmol), 4-flurothiophenol (2.0 mmol), 10 mol% CuI, 20 mol% L-proline, and 1.2 equiv of K_2CO_3 in 10 ml of 95% EtOH at reflux under N_2 atmosphere.

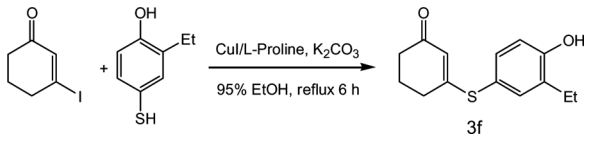
[b]Isolated yields.

[c]Functional group is –SH.

tolerates a wide range of functional groups and substrates. We have also demonstrated the ability to couple both arylthiols and heterocyclic thiols to vinyl iodide and the catalytic efficiency of different amino acids. Additionally, the reaction avoids the use of high-boiling-point solvents such as DMF, DMSO, and $[Bmim]BF_4$ and does not require the use of expensive palladium and/or air-sensitive additives.

EXPERIMENTAL

^{1}H NMR spectra were recorded on Bruker Avance-300 spectrometer with TMS as internal standard. IR spectra were determined on Vector-55



Scheme 2.

Table 3. Effect of different α-amino acids in the coupling of 3-iodo-cyclohexenone with 4-flurothiophenol reflux in 95% ethanol

Entry	Additive	Time (h)	Yield (%)
1	L-Proline	6	92
2	L-Glycine	8	84
3	N-Methylglycine	8	85
4	l-Lysine	9	73
5	Ethane-1,2-diamine	8	52
6	Triphenyl-phosphane	8	75
7	None	8	25
8	None	16	55

instrument. Elemental analyses were conducted using a Yanaco MT-5CHN elemental analyzer. Silica gel GF254 was used for analytical and preparative thin-layer chromotography (TLC). All products were characterized by comparison with authentic samples using IR, ^{1}H NMR, and MS.

General Procedure for the Synthesis of 3a–l

We placed 10 mL of 95% ethanol and 2.4 mmol of K_2CO_3 in a 25-mL beaker, refluxing for 30 min under N_2 atmosphere and then cooling to room temperature. Then 2 mmol of 3-iodo-cyclohexenone, 2 mmol of thiophenol, 10 mol% CuI, and 20 mol% L-proline were added to the mixture. The mixture in beaker was allowed to stir for a few minutes until it was homogeneous, and then it was refluxed 4–6 h. The cooled mixture was filtered with suction, the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel with cyclohexane and ethyl acetate (V:V = 10:1) as eluent.

Data

3-(4-Fluoro-phenylsulfanyl)-cyclohex-2-enone (3a): yellow oil. ^{1}H NMR ($CDC1_3$): δ = 7.43–7.49 (m, 2H), 7.09–7.16 (m, 2H), 5.41 (s, 1H), 2.50–2.54 (t, J = 6.14, 2H), 2.36–2.38 (t, J = 6.91, 2H), 2.01–2.09 (m, 2H); IR (film): ν = 3002, 1650, 1570, 1405, 1285, 978; MS (70 eV) m/z (%): 222 (M^+, 18), 154 (100), 109 (78), 77 (65), 58 (45), 28 (55). Anal. calcd. for $C_{12}H_{11}FOS$: C, 64.84; H, 4.99; found: C, 64.76; H, 4.88.

3-(3-Fluoro-phenylsulfanyl)-cyclohex-2-enone (3b): yellow oil. ^{1}H NMR ($CDC1_3$): δ = 7.51–7.59 (m, 3H), 7.19–7.24 (m, 1H), 5.35 (s, 1H),

2.45–2.50 (t, $J = 6.18$, 2H), 2.32–2.36 (t, $J = 6.85$, 2H), 2.03–2.12 (m, 2H); IR (film): $\nu = 2982$, 1652, 1571, 1450, 780; MS (70 eV) m/z (%): 222 (M^+, 36), 153 (100), 108 (58), 76 (75), 58 (42), 28 (85). Anal. calcd. for $C_{12}H_{11}FOS$: C, 64.84; H, 4.99; found: C, 64.97; H, 4.90.

3-(2-Fluoro-phenylsulfanyl)-cyclohex-2-enone (3c): yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.53$–7.62 (m, 3H), 7.16–7.26 (m, 1H), 5.23 (s, 1H), 2.46–2.52 (t, $J = 6.15$, 2H), 2.36–2.42 (t, $J = 6.81$, 2H), 2.13–2.18 (m, 2H); IR (film): $\nu = 3109$, 1650, 1500, 1450, 958, 750; MS (70 eV) m/z (%): 222 (M^+, 75), 153 (100), 111 (45), 76 (55), 58 (25), 28 (65). Anal. calcd. for $C_{12}H_{11}FOS$: C, 64.84; H, 4.99; found: C, 64.77; H, 5.09.

3-(3,5-Difluoro-phenylsulfanyl)-cyclohex-2-enone (3d): yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.03$–7.07 (m, 2H), 6.89–6.95 (m, 1H), 5.53 (s, 1H), 2.51–2.55 (m, 2H), 2.38–2.43 (m, 2H), 2.03–2.11 (m, 2H); IR (film): $\nu = 3082$, 2945, 1650, 1574, 1427, 1285, 1119, 983, 671; MS (70 eV) m/z (%): 241 ($[M+1]^+$, 11), 240 (M^+, 79), 172 (100), 112 (68), 95 (82), 72 (75), 58 (65), 15 (46). Anal. calcd. for $C_{12}H_{10}F_2OS$: C, 59.99; H, 4.20; found: C, 60.17; H, 4.19.

3-(4-Trifluoromethoxy-phenylsulfanyl)-cyclohex-2-enone (3e): yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.51$–7.54 (q, $J = 8.7$, 2H), 7.26–7.28 (q, $J = 8.5$, 2H), 5.46 (s, 1H), 2.51–2.55 (t, $J = 6.14$, 2H), 2.36–2.41 (t, $J = 6.81$, 2H), 2.04–2.10 (m, 2H); IR (film): $\nu = 3182$, 2900, 1580, 1524, 1401, 985; MS (70 eV) m/z (%): 289 ($[M+1]^+$, 13), 288 (M^+, 82), 234 (85), 220 (100), 90 (65), 65 (55). Anal. calcd. for $C_{13}H_{11}F_3O_2S$: C, 54.16; H, 3.85; found: C, 54.24; H, 3.91.

3-(3-Ethyl-4-hydroxy-phenylsulfanyl)-cyclohex-2-enone (3f): white solid, mp 67–69 °C. ^1H NMR ($CDC1_3$): $\delta = 8.24$ (s, 1H), 7.18 (s, 1H), 6.93–7.00 (m, 1H), 6.59–6.61 (dd, $J = 8.2$, 1H), 5.47 (s, 1H), 2.48–2.59 (m, 4H), 2.22–2.29 (m, 2H), 1.94–2.04 (m, 2H), 1.09–1.31 (m, 3H); IR (KBr): $\nu = 3321$, 3107, 2956, 1567, 1485, 1420, 976; MS (70 eV) m/z (%): 249 ($[M+1]^+$, 8), 248 (M^-, 100), 179 (89), 104 (54), 91 (76), 64 (45), 58 (45), 28 (35). Anal. calcd. for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49; found: C, 67.84; H, 6.50.

3-(4-Bromo-benzylsulfanyl)-cyclohex-2-enone (3 g): yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.40$–7.48 (dd, $J = 8.02$, 2H), 7.19–7.29 (dd, $J = 6.85$, 2H), 5.90 (s, 1H), 3.98 (s, 2H), 2.36–2.48 (m, 4H), 2.00–2.08 (m, 2H); IR (film): $\nu = 3044$, 2934, 2858, 1645, 1565, 1186, 886; MS (70 eV) m/z (%): 298 (M^+, 100), 296 (89), 230 (87), 228 (65), 203 (72), 170 (82), 91 (87), 72 (53), 64 (35), 58 (55), 28 (51). Anal. calcd. for $C_{13}H_{13}BrOS$: C, 52.53; H, 4.41; found: C, 52.44; H, 4.50.

3-(2-Isopropyl-phenylsulfanyl)-cyclohex-2-enone (3 h): yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.40$–7.42 (m, 3H), 7.19–7.21 (m, 1H), 5.34 (s, 1H), 3.45–3.51 (m, 1H), 2.55 (t, $J = 6.57$, 2H), 2.34–2.36 (m, $J = 6.98$, 2H), 2.04 (m, 2H), 1.21 (s, 3H), 1.18 (s, 3H); IR (film): $\nu = 2956$, 2923, 1655, 1572,

1380, 1000, 880, 749; MS (70 eV) m/z (%): 247 ($[M+1]^+$, 17), 246 (M^+, 100), 194 (56), 178 (84), 118 (76), 91 (77), 72 (45), 58 (55), 28 (48), 15 (68). Anal. calcd. for $C_{15}H_{18}OS$: C, 73.13; H, 7.36; found: C, 73.03; H, 7.40.

3-(2,6-Dimethyl-phenylsulfanyl)-cyclohex-2-enone (3i): yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.04$–7.28 (m, 3H), 5.24 (s, 1H), 2.53–2.62 (t, $J = 6.53$, 2H), 2.38 (s, 6H), 2.35–2.37 (t, $J = 6.64$, 2H), 2.01–2.16 (m, 2H); IR (film): $\nu = 3356$, 3092, 2921, 1658, 1523, 1380, 840, 723; MS (70 eV) m/z (%): 233 ($[M+1]^+$, 8), 232 (M^+, 62), 179 (51), 164 (100), 105 (74), 104 (71), 92 (73), 58 (42), 15 (61). Anal. calcd. for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; found: C, 72.19; H, 6.86.

3-(2-Ethoxy-phenylsulfanyl)-cyclohex-2-enone (3j): yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.37$–7.44 (m, 2H), 6.92–6.98 (t, $J = 7.80$, 2H), 5.46 (s, 1H), 4.03–4.10 (dd, 2H), 2.51–2.53 (t, $J = 6.01$, 2H), 2.37–2.55 (t, $J = 6.27$, 2H), 1.99–2.08 (m, 2H), 1.18–1.42 (m, 3H); IR (film): $\nu = 3247$, 3021, 1651, 1571, 1381, 1027, 882; MS (70 eV) m/z (%): 249 ($[M+1]^+$, 11), 248 (M^+, 71), 196 (77), 180 (100), 121 (57), 91 (78), 66 (65), 58 (55), 28 (54). Anal. calcd. for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49; found: C, 67.69; H, 6.56.

3-(2,6-Bis-trifluoromethyl-phenylsulfanyl)-cyclohex-2-enone (3k): yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.96$ (s, 1H), 7.40–7.48 (m, 2H), 5.40 (s, 1H), 2.55–2.62 (m, 2H), 2.41–2.43 (m, 2H), 2.06–2.14 (m, 2H); IR (film): $\nu = 3052$, 2942, 1649, 1584, 1434, 1106, 905, 702; MS (70 eV) m/z (%): 341 ($[M+1]^+$, 6), 340 (M^+, 54), 287 (65), 272 (100), 212 (52), 196 (77), 121 (57), 94 (78), 66 (65), 58 (55). Anal. calcd. for $C_{14}H_{10}F_6OS$: C, 49.41; H, 2.96; found: C, 49.29; H, 2.86.

3-(3-Ethyl-phenylsulfanyl)-cyclohex-2-enone (3l):yellow oil. ^1H NMR ($CDC1_3$): $\delta = 7.27$–7.29 (m, 1H), 7.21–7.24 (m, 1H), 6.85–6.89 (m, 2H), 5.12 (s, 1H), 2.63–2.65 (m, 2H), 2.31–2.43 (m, 4H), 1.96–2.04 (m, 2H), 1.28–1.30 (m, 3H); IR (film): $\nu = 3258$, 3088, 2902, 1608, 1545, 1104, 924, 701; MS (70 eV) m/z (%): 233 ($[M+1]^+$, 14), 232 (M^+, 34), 179 (67), 164 (100), 106 (54), 91 (68), 58 (51), 28 (65). Anal. calcd. for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; found: C, 72.31; H, 6.85.

3-(4-Amino-2-fluoro-phenylsulfanyl)-cyclohex-2-enone (3m): ^1H NMR ($CDC1_3$): $\delta = 7.07$–7.12 (m, 1H), 6.98–7.02 (m, 1H), 6.61–6.67 (m, 1H), 5.42 (s, 1H), 3.72 (b 2H), 2.58–2.61 (m, 2H),2.35–2.38 (m, 2H), 2.02–2.05 (m, 2H); IR (film): $\nu = 3458$, 3356, 3012, 2812, 1635, 1505, 924, 771; MS (70 eV) m/z (%): 238 ($[M+1]^+$, 13), 237 (M^+, 52), 184 (78), 168 (100), 110 (84), 92 (46), 65 (28), 58 (59). Anal. calcd. for $C_{12}H_{12}FNOS$: C, 60.74; H, 5.10; found: C, 61.06; H, 5.05.

3-(Thiazol-2-ylsulfanyl)-cyclohex-2-enone (3n): ^1H NMR ($CDC1_3$): $\delta = 7.97$–7.98 (d, $J = 3.45$, 1H), 7.63–7.64 (d, $J = 3.42$, 1H), 5.74 (s, 1H), 2.42–2.55 (t, 2H), 2.37–2.39 (t, 2H), 2.03–2.11 (m, 2H); IR (film): $\nu = 3052$, 2919, 1708, 1635, 1505, 865, 701; MS (70 eV) m/z (%): 212

([M + 1]$^+$, 6), 211 (M$^+$, 34), 158 (84), 142 (100), 121 (46), 61 (28), 58 (72). Anal. calcd. for $C_9H_9NOS_2$: C, 51.16; H, 4.29; found: C, 51.21; H, 4.15.

3-(Pyrimidin-2-ylsulfanyl)-cyclohex-2-enone (3o): $\delta = 8.77$–8.82 (m, 2H), 7.23–7.25 (m, 1H), 5.72 (s, 1H), 2.72–2.76 (t, 2H), 2.17–2.21 (t, 2H), 1.95–1.99 (m, 2H); IR (film): $\nu = 3055$, 2978, 1713, 1652, 1506, 885, 775; MS (70 eV) m/z (%): 207 ([M + 1]$^+$, 14), 206 (M$^+$, 100), 154 (68), 137 (56), 111 (48), 58 (63), 15 (55). Anal. calcd. for $C_{10}H_{10}N_2OS$: C, 58.23; H, 4.89; found: C, 58.21; H, 4.85.

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