



CuI catalyzed-novel one-pot synthesis of aryl alkenyl thioethers through Ullmann-type coupling reactions using carbon disulfide as a sulfur surrogate in the presence of nitroalkanes and aryl iodides

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ARTICLE INFO

Article history:

Received 22 February 2018

Revised 25 March 2018

Accepted 30 March 2018

Available online 1 April 2018

Keywords:

Copper(I) iodide

L-Proline

Ullmann-type coupling

S-arylation

CS₂

ABSTRACT

A mild, general and efficient copper-catalyzed system for C-S bond formation is developed. With CuI as catalyst and L-Proline as ligand, the S-arylation of nitroalkane-CS₂ adducts with aryl iodides were performed under mild conditions to give the corresponding products in good to excellent yields.

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Introduction

Catalytic procedure for C-S bond formation are substantial due to the great demand in pharmaceutical industry,¹ organic synthesis² and material sciences.³ As an example, the aryl sulfide unit is a usual motif found in many drugs used for treating a variety of illnesses, such as parkinson, alzheimer, cancer, diabetes, HIV (human immunodeficiency virus) infection, and inflammation.⁴ Therefore, the enhancing effective methods for S-arylation is an interest in organic chemistry. Since Migita first reported the palladium-catalyzed C-S bond formation to produce thioethers,^{5,6} the transition metal-catalyzed (TMC) C-S cross coupling reaction has not been studied robustly compared to the other carbon heteroatom bonds such as C-N, C-O, C-P, despite the powerful coordinative nature of the sulfur atom. Moreover, it works as a toxicant and completely represses the activity of the catalyst.⁷ These compounds are generally derived by Ullmann-type coupling S-arylation reactions at high temperatures (approximately 200 °C) and often need the consumption of stoichiometric quantity of copper reagents, which limits their further utilization.⁸ Thus, to prevail these problems, a mild, simple, economically affordable and effective catalytic system is ever hoped for this process.

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The additional reaction between nitroalkane and carbon disulfide has been reported by Jensen.⁹ This reaction is carried out in the presence of a base at ambient temperature with high efficiency. Using this strategy, a strong nucleophile is formed which can produce C-S bond. Consequently, during our continuing screening for the formation of C-S bond, we have investigated copper-catalyzed S-arylation. In this paper, we report a catalytic system, which can catalyze Ullmann-type coupling reaction of nitroalkane, CS₂ and aryl iodide. This study provides a new and cost effective method for the synthesis of aryl alkenyl thioethers. The novelty of this procedure is due to its operational simplicity, since the reaction can be performed with analytical grade solvents in open environment without special precautions. Furthermore, one-pot reaction and mild conditions were applied. All the newly synthesized products were fully characterized by their IR, Mass, CHN, ¹H NMR and ¹³C NMR spectra.

Experimental

General procedure

A mixture of nitroethane or nitromethane **1** (1 mmol), Cs₂CO₃ (1.5 mmol) and CS₂ (152 mg, 2 mmol) in CH₃CN (2 mL) was stirred for 10 min at r.t. Then this mixture was added to a stirred soln. of aryl iodide **2** (1 mmol), CuI (10 mol%) and L-Proline (10 mol%) in

CH₃CN (2 mL), and heated at 60 °C for 2 h. After completion of the reaction (ca. 2 h; TLC (AcOEt/hexane 1:2) monitoring), the mixture was filtered and washed with CH₂Cl₂ (2 mL). Then solution was concentrated and purified by flash column chromatography (SiO₂; hexane/AcOEt 2:1) to give products **3**.

Analytical data

2-nitro-1-(phenylthio)prop-1-ene-1-thiol (Table 2, entry 1)

Yield: 0.190 g (84%). Colorless liquid. IR: 1650, 1496, 1530, 1374, 1241, 1171 and 1104. ¹H NMR (400.1 MHz, CDCl₃): δ = 2.87 (s, 3H, CH₃), 6.98–7.19 (br, 1H, SH), 7.62 (t, *J* = 7.6 Hz, 2H, 2CH), 7.74 (t, *J* = 7.6 Hz, 1H, CH), 8.05 (d, *J* = 7.7 Hz, 2H, 2CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 26.9 (CH₃), 100.2 (CCH₃), 127.4 (2CH), 130.1 (2CH), 135.7 (CH), 145.0 (C), 170.9 (S₂C). EI-MS: *m/z* (%) = 227 (M⁺, 17), 181 (19), 149 (67), 125 (14), 103 (35), 91 (39), 77 (1 0 0), 65 (47). Anal. Calcd for C₉H₉NO₂S₂: C, 47.56; H, 3.99; N, 6.16. Found: C, 47.54; H, 3.98; N, 6.18.

1-(4-nitrophenylthio)-2-nitroethenethiol (Table 2, entry 2)

Yield: 0.231 g (90%). Yellow powder, mp 158 °C. IR: 1597, 1461, 1530, 1367, 1257, 1170 and 1099. ¹H NMR (400.1 MHz, CDCl₃): δ = 6.10 (s, 1H, CH), 7.00–7.15 (br, 1H, SH), 7.42 (d, *J* = 8.4 Hz, 2H, 2CH), 7.94 (d, *J* = 8.4 Hz, 2H, 2CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 110.0 (CH), 126.2 (C), 128.1 (2CH), 131.4 (2CH), 142.8 (C), 172.8 (S₂C). EI-MS: *m/z* (%) = 257 (M⁺, 6), 230 (4), 211 (12), 186 (7), 166 (13), 162 (19), 155 (1 0 0), 148 (30), 140 (14), 122 (18), 85 (19), 77 (47), 64 (37), 62 (37). Anal. Calcd for C₈H₆N₂O₄S₂: C, 37.20; H, 2.34; N, 10.85. Found: C, 37.22; H, 2.35; N, 10.83.

1-(4-bromophenylthio)-2-nitroethenethiol (Table 2, entry 3)

Yield: 0.239 g (82%). White powder, mp 102 °C. IR: 1575, 1497, 1370, 1267, 1171 and 1104. ¹H NMR (400.1 MHz, CDCl₃): δ = 6.02 (s, 1H, CH), 6.98–7.01 (br, 1H, SH), 7.40 (d, *J* = 6.6 Hz, 2H, 2CH), 7.89 (d, *J* = 6.7 Hz, 2H, 2CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 110.1 (CH), 125.8 (C), 127.4 (2CH), 130.7 (2CH), 132.5 (C), 168.8 (S₂C). EI-MS: *m/z* (%) = 292 (M⁺, 14), 244 (8), 231 (10), 200 (27), 186 (31), 165 (16), 154 (1 0 0), 145 (14), 121 (14), 91 (49), 77 (47). Anal. Calcd for C₈H₆BrNO₂S₂: C, 32.89; H, 2.07; N, 4.79. Found: C, 32.90; H, 2.05; N, 4.81.

1-(4-bromophenylthio)-2-nitroprop-1-ene-1-thiol (Table 2, entry 4)

Yield: 0.269 g (88%). White powder, mp 123 °C. IR: 1600, 1503, 1404, 1331, 1264, 1171 and 1104. ¹H NMR (400.1 MHz, CDCl₃): δ = 2.88 (s, 3H, CH₃), 6.74–6.96 (br, 1H, SH), 7.83 (d, *J* = 6.6 Hz, 2H, 2CH), 7.91 (d, *J* = 6.7 Hz, 2H, 2CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 27.0 (CH₃), 100.2 (CCH₃), 127.5 (C), 128.0 (2CH), 130.7 (2CH), 134.0 (C), 171.2 (S₂C). EI-MS: *m/z* (%) = 306 (M⁺, 22), 258 (25), 231 (42), 185 (11), 154 (1 0 0), 149 (87), 140 (86), 101 (59), 79 (67), 73 (84). Anal. Calcd for C₉H₈BrNO₂S₂: C, 35.30; H, 2.63; N, 4.57. Found: C, 35.28; H, 2.62; N, 4.59.

1-(4-methoxyphenylthio)-2-nitroprop-1-ene-1-thiol (Table 2, entry 5)

Yield: 0.177 g (69%). Yellow powder, mp 131 °C. IR: 1596, 1530, 1461, 1367, 1323, 1257, 1170 and 1098. ¹H NMR (400.1 MHz, CDCl₃): δ = 2.46 (s, 3H, CH₃), 3.69 (s, 3H, OCH₃), 6.40–6.61 (br, 1H, SH), 7.38 (d, *J* = 7.5 Hz, 2H, 2CH), 7.90 (d, *J* = 7.5 Hz, 2H, 2CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 26.4 (CH₃), 55.9 (OCH₃), 100.0 (CCH₃), 124.0 (C), 127.6 (2CH), 129.8 (C), 130.7 (2CH), 172.1 (S₂C). EI-MS: *m/z* (%) = 257 (M⁺, 22), 230 (17), 163 (24), 148 (94), 140 (62), 118 (19), 107 (1 0 0), 73 (62), 58 (73). Anal. Calcd for C₁₀H₁₁NO₃S₂: C, 46.67; H, 4.31; N, 5.44. Found: C, 46.69; H, 4.32; N, 5.41.

1-(*p*-tolylthio)-2-nitroprop-1-ene-1-thiol (Table 2, entry 6)

Yield: 0.180 g (75%). White powder, mp 140 °C. IR: 1567, 1531, 1370, 1324, 1255, 1174 and 1098. ¹H NMR (400.1 MHz, CDCl₃): δ = 2.35 (s, 3H, CH₃), 3.07 (s, 3H, CH₃), 6.61–6.95 (br, 1H, SH), 7.38 (d, *J* = 7.8 Hz, 2H, 2CH), 7.89 (d, *J* = 7.7 Hz, 2H, 2CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 23.6 (CH₃), 29.3 (CH₃), 100.4 (CCH₃), 127.0 (C), 127.4 (2CH), 129.6 (C), 130.7 (2CH), 170.0 (S₂C). EI-MS: *m/z* (%) = 241 (M⁺, 39), 216 (21), 201 (25), 170 (39), 159 (1 0 0), 156 (66), 144 (64), 124 (41), 118 (83), 91 (71), 77 (93). Anal. Calcd for C₁₀H₁₁NO₂S₂: C, 49.77; H, 4.59; N, 5.80. Found: C, 49.78; H, 4.57; N, 5.82.

1-(*p*-tolylthio)-2-nitroethenethiol (Table 2, entry 7)

Yield: 0.163 g (72%). White powder, mp 120 °C. IR: 1690, 1597, 1510, 1397, 1267, 1168 and 1098. ¹H NMR (400.1 MHz, CDCl₃): δ = 2.68 (s, 3H, CH₃), 6.00 (s, 1H, CH), 6.80–6.99 (br, 1H, SH), 7.40 (d, *J* = 6.5 Hz, 2H, 2CH), 7.92 (d, *J* = 6.7 Hz, 2H, 2CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 30.6 (CH₃), 111.0 (CH), 126.6 (C), 127.4 (2CH), 129.7 (C), 130.6 (2CH), 171.1 (S₂C). EI-MS: *m/z* (%) = 227 (M⁺, 37), 195 (18), 181 (41), 168 (25), 116 (39), 103 (43), 91 (87), 77 (1 0 0), 65 (62). Anal. Calcd for C₉H₉NO₂S₂: C, 47.56; H, 3.99; N, 6.16. Found: C, 47.58; H, 4.01; N, 6.18.

1-(4-nitrophenylthio)-2-nitroprop-1-ene-1-thiol (Table 2, entry 8)

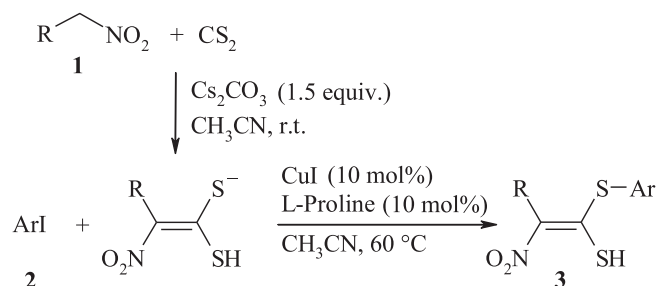
Yield: 0.247 g (91%). Yellow powder, mp 170 °C. IR: 1690, 1598, 1539, 1441, 1390, 1373 and 1097. ¹H NMR (400.1 MHz, CDCl₃): δ = 2.90 (s, 3H, CH₃), 6.98–7.01 (br, 1H, SH), 7.40 (d, *J* = 8.0 Hz, 2H, 2CH), 7.92 (d, *J* = 8.0 Hz, 2H, 2CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 28.0 (CH₃), 100.1 (CCH₃), 127.5 (2CH), 130.6 (2CH), 133.1 (C), 137.2 (C), 171.2 (S₂C). EI-MS: *m/z* (%) = 272 (M⁺, 22), 246 (10), 226 (22), 201 (20), 197 (16), 174 (8), 166 (14), 150 (23), 149 (1 0 0), 122 (12), 89 (16), 74 (22). Anal. Calcd for C₉H₈N₂O₄S₂: C, 39.70; H, 2.96; N, 10.29. Found: C, 39.71; H, 2.94; N, 10.28.

1-(2-nitrophenylthio)-2-nitroethenethiol (Table 2, entry 9)

Yield: 0.207 g (80%). Yellow powder, mp 144 °C. IR: 1680, 1597, 1561, 1360, 1323, 1257 and 1099. ¹H NMR (400.1 MHz, CDCl₃): δ = 6.00 (s, 1H, CH), 6.69–6.75 (br, 1H, SH), 7.29–7.34 (m, 2H, 2CH), 7.39 (d, *J* = 7.0 Hz, 1H, CH), 7.92 (d, *J* = 7.1 Hz, 1H, CH). ¹³C NMR (100.8 MHz, CDCl₃): δ = 109.0 (CH), 122.5 (C), 127.5 (CH), 128.7 (CH), 129.2 (C), 130.7 (CH), 132.5 (CH), 172.8 (S₂C). EI-MS: *m/z* (%) = 259 (M⁺, 38), 198 (33), 189 (33), 173 (24), 153 (1 0 0), 141 (61), 122 (29), 97 (78), 89 (66), 64 (71). Anal. Calcd for C₈H₆N₂O₄S₂: C, 37.20; H, 2.34; N, 10.85. Found: C, 37.21; H, 2.35; N, 10.83.

Results and discussion

We report a one-pot synthesis of aryl alkenyl thioethers using aryl iodides and carbon disulfide as a sulfur substitute in the presence of nitroalkane, catalyzed by copper(I) iodide in acetonitrile as solvent resulting in good to excellent yields (Scheme 1).



Scheme 1. CuI-catalyzed S-arylation of nitroalkane-CS₂ adduct.

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