Note

Diiodination of Alkynes in Supercritical Carbon Dioxide

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A general, green and efficient method for the synthesis of *trans*-diiodoalkenes in CO_2 (sc) has been developed. *Trans*-diiodoalkenes were obtained stereospecifically in quantitative yields via diiodination of both electron-rich and electron-deficient alkynes in the presence of KI, $Ce(SO_4)_2$ and water in supercritical carbon dioxide [CO_2(sc)] at 40 ℃.

Keywords *trans*-diiodoalkenes, alkynes, diiodination, supercritical carbon dioxide

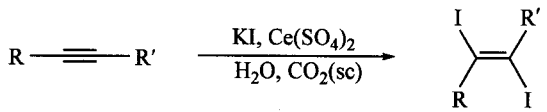
Introduction

Supercritical carbon dioxide [CO_2(sc)] is rapidly becoming alternative reaction media for conventional organic reaction.[1] The advantages of reactions in CO_2(sc) include the high solubility of gaseous reactants, rapid diffusion of solutes, and weakening of the solvation around the reacting species. Recent progress has shown that CO_2(sc) can be used instead of conventional organic solvents in various transition metal catalyzed transformations.[2]

Diiodoalkenes are valuable intermediates in organic synthesis.[3] There are several ways to synthesize diiodoalkenes[4-8] such as alumina,[4] florisil[5] or CuI[6]-assisted iodination of alkynes, direct addition of iodine to alkynes,[7] and using electropositive iodonium species in the presence of iodide ion.[3c,8] The stereoselection of diiodoalkenes depends upon the reaction conditions. Generally, (*E*)-isomers are obtained as the major product. In addition, I_2 or IX was used as an iodide resource and harmful solvents such as CH_3CN, CH_2Cl_2, MeOH and petroleum ether were used in all cases. Thus, a study for a new iodide resource and a green solvent for diiodination of alkynes is important. In this paper, we demonstrated that using CO_2(sc) as the reaction media diiodination of alkynes with KI and $Ce(SO_4)_2$ could be carried out efficiently in the presence of H_2O (Scheme 1).

Firstly, we chose reaction of phenylacetylene **1a** with KI and $Ce(SO_4)_2$ in CO_2(sc) as a model reaction system for the optimum studies. Experimental results of the diiodination of phenylacetylene (**1a**) are summarized in

Scheme 1



1 **2**

Table 1. Phenylacetylene (**1a**) (1 mmol) reacted with KI (2.05 mmol) and $Ce(SO_4)_2$ (2 mmol) in CO_2 (14 MPa) at 40 ℃ for 4 h to give 59% of *trans*-1,2-diiodostyrene (**2a**). Remarkably, yield of *trans*-1,2-diiodostyrene (**2a**) was increased to quantitative in the presence of H_2O (0.1 mL). The presence of $Ce(SO_4)_2$ was critical: in its absence, the reaction could not proceed. The *trans* stereochemistry of diiodoalkene **2a** was assigned on the basis of the chemical shift of the olefinic proton in their ^1H NMR spectra, which were identical to those reported in the literature for the *trans*-isomers.[1c,3-5] Basing on above results, the optimum reaction conditions for the diiodination were: alkyne **1** (1 mmol), $Ce(SO_4)_2$ (2 mmol), KI (2.05 mmol), and H_2O (0.1 mL) in CO_2 (14 MPa) at 40 ℃.

Table 1 Diiodination of alkynes in supercritical carbon dioxide[a]

Entry	Alkyne (**1**)	Reaction time (h)	Isolated yield of **2** (%)
1[b]	PhC≡CH (**1a**)	4	59
2	PhC≡CH (**1a**)	4	quantitative
3[c]	PhC≡CH (**1a**)	4	—
4	$C_8H_{17}C$≡CH (**1b**)	4	quantitative
5	C_3H_7C≡CC_3H_7 (**1c**)	4	quantitative
6	CH_3C≡CCOOMe (**1d**)	6	quantitative
7	HC≡CCOOEt (**1e**)	6	quantitative

[a] Reaction conditions: alkyne **1** (1 mmol), $Ce(SO_4)_2$(2 mmol), KI (2.05 mmol), and H_2O (0.1 mL) in CO_2 (14 MPa) at 40 ℃. [b] In the absence of H_2O, the conversion of phenylacetylene was 100% which was detected by GC analysis. [c] In the absence of $Ce(SO_4)_2$.

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133 (29), 119 (42), 105 (56), 91 (100).

Benzylmethyl(undec-2-ynyl)amine (**6**) Oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.35—7.22 (m, 5H), 3.55 (s, 2H), 3.26 (t, J = 2.0 Hz, 2H), 2.30 (s, 3H), 2.26—2.20 (m, 2H), 1.59—1.28 (m, 12H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.6, 129.2, 128.2, 127.1, 85.8, 74.6, 60.2, 45.5, 41.8, 31.8, 29.2, 29.1, 29.0, 28.9, 22.6, 18.7, 14.0; IR (film) ν: 2260 (C≡C) cm^{-1}; MS (70 eV) *m/z* (%): 271 (M^+, 7), 194 (25), 158 (22), 120 (18), 91 (100). Anal. calcd for $C_{19}H_{29}N$: C 84.07, H 10.77, N 5.16; found C 83.96, H 10.85, N 5.19.

Benzylmethyl(3-phenyl-prop-2-ynyl)amine (**7a**) Oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.48—7.44 (m, 2H), 7.38—7.23 (m, 8H), 3.62 (s, 2H), 3.49 (s, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.3, 131.6, 129.1, 128.1, 127.9, 127.1, 123.2, 85.6, 84.3, 60.1, 45.6, 41.8; IR (film) ν: 2235 (C≡C) cm^{-1}; MS (70 eV) *m/z* (%): 235 (M^+, 18), 158 (41), 144 (27), 115 (100), 91 (64). Anal. calcd for $C_{17}H_{17}N$: C 86.77, H 7.28, N 5.95; found C 86.66, H 7.43, N 6.01.

Benzylmethyl(3-p-tolyl-prop-2-ynyl)amine (**7b**) Oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.37—7.24 (m, 7H), 7.09 (d, J = 7.94 Hz, 2H), 3.62 (s, 2H), 3.49 (s, 2H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.4, 137.9, 131.5, 129.1, 128.9, 128.2, 127.1, 120.2, 85.7, 83.6, 60.2, 45.7, 41.9, 21.3; IR (film) ν: 2247 (C≡C) cm^{-1}; MS (70 eV) *m/z* (%): 249 (M^+, 17), 172 (32), 158 (36), 129 (100), 91 (73). Anal. calcd for $C_{18}H_{19}N$: C 86.70, H 7.68, N 5.62; found C 86.42, H 7.60, N 5.57.

Benzylmethyl [3-(4-*chlorophenyl*)-*prop*-2-*ynyl*] *amine* (**7c**) Oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.38—7.24 (m, 9H), 3.61 (s, 2H), 3.48 (s, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.2, 133.9, 132.8, 129.1, 128.5, 128.2, 127.1, 121.6, 85.5, 84.4, 60.2, 45.6, 41.9; IR (film) ν: 2251 (C≡C) cm^{-1}; MS (70 eV) *m/z* (%): 271, 269 (M^+, 6, 17), 192 (30), 178 (32), 158 (14), 149 (91), 132 (15), 114 (17), 91 (100). Anal. calcd for $C_{17}H_{16}NCl$: C 75.69, H 5.98, N 5.19; found C 75.53, H 6.06, N 5.33.

Benzylmethyl[3-(2-*nitrophenyl*)-*prop*-2-*ynyl*] *amine* (**7d**) Oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.01 (dd, J = 8.21, 1.08 Hz, 1H), 7.64—7.51 (m, 2H), 7.45—7.26 (m, 6H), 3.69 (s, 2H), 3.58 (s, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 149.7, 138.2, 134.8, 132.6, 129.1, 128.3, 128.2, 127.1, 124.4, 118.4, 93.3, 80.9, 59.9, 45.6, 41.9; IR (film) ν: 2268 (C≡C) cm^{-1}; MS (70 eV) *m/z* (%): 280 (M^+, 4), 263 (14), 203 (10), 189 (6), 144 (18), 132 (20), 120 (19), 104 (16), 91 (100). Anal. calcd for $C_{17}H_{16}N_2O_2$: C 72.84, H 5.75, N 9.99; found C 72.63, H 5.82, N 9.91.

Benzylmethyl [3-(4-*bromophenyl*)-*prop*-2-*ynyl*] *amine* (**7e**) Oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.42 (d, J = 7.76 Hz, 2H), 7.28 (d, J = 7.96 Hz, 2H), 7.18—7.04 (m, 5H), 3.62 (s, 2H), 3.15 (s, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.3, 135.8, 132.4, 129.1, 128.4, 128.1, 127.0, 121.4, 85.8, 84.6, 60.5, 45.7, 41.9; IR (film) ν: 2257 (C≡C) cm^{-1}; MS (70 eV) *m/z* (%): 315, 317 (M^+, 8, 9), 238 (23), 224 (27), 204 (11), 160 (67), 132 (15), 115(17), 91 (100). Anal. calcd for $C_{17}H_{16}NBr$: C 64.98, H 5.13, N 4.46; found C 65.12, H 5.01, N 4.59.

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9 The reaction solution turned into red quickly, then slowly discolored to colorless in the end.

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