Supporting Information

Title: Inter- and Intramolecular Radical Couplings of Ene-Ynes or Halo-Alkenes Promoted by $\text{InCl}_3/\text{MeONa}/\text{Ph}_2\text{SiH}_2$ System

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General:

IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All ^1H and ^{13}C -NMR spectra were recorded with a JEOL JNM-GSX-270 (270 and 67 MHz, respectively) or JEOL JMT-400/54/SS (400 and 100 MHz, respectively) in deuteriochloroform (CDCl_3) containing 0.03% (w/v) of tetramethylsilane. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. Column chromatography was performed by using Fuji Davison silica gel FL-100DX.

A typical experimental procedure of the reaction of alkyne (enyne):

A 10 mL of round bottom flask charged with InCl_3 (0.221 g, 1.0 mmol) was dried by heating at 110°C under reduced pressure for 1 h. After nitrogen was filled, THF (2 mL) was added to dissolve InCl_3 . NaOMe (1.0 mmol) was added to the mixture, and stirred at rt for 0.5 h. Then Ph_2SiH_2 (2.0 mmol), alkyne (1.0 mmol) and 1M Et_3B in hexane (0.1 mL) were added, and the resulting mixture was stirred at rt for 2 h. After 1N HCl aq was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over MgSO_4 and concentrated. Purification was performed by column chromatography eluting with hexane/EtOAc. Further purification was performed by TLC eluting with hexane/ Et_2O or distillation under reduced pressure. Product was determined by ^1H NMR or GC.

4-Benzyl-3-methylene-tetrahydro-furan (4a)

Reference : Oh, C. H. et al. *Tetrahedron* **2001**, 57, 1723-1729.

Colorless oil (Isolated yield 89%)

IR (neat) $1065\text{ (C-O-C)}\text{ cm}^{-1}$

^1H NMR (CDCl_3 , 400 MHz) δ 7.31-7.18 (m, 5H), 4.97 (dd, $J = 4.1$ and 1.9 Hz, 1H), 4.91 (dd, $J = 4.6$ and 2.4 Hz, 1H), 4.37 (t, $J = 2.0$ Hz, 2H), 3.87 (dd, $J = 8.7$ and 6.6 Hz, 1H), 3.60 (dd, $J = 8.7$ and 5.9 Hz, 1H), 2.99-2.92 (m, 2H), 2.64 (dd, $J = 15.2$ and 11.1 Hz, 1H)

^{13}C NMR (CDCl_3 , 100.6 MHz) δ 151.30, 139.97, 128.76, 128.40, 126.17, 104.04, 73.52, 71.59, 45.23, 38.75

MS (EI) m/z 91 (CH_2Ph , 88), 83 ($\text{M}^+ - \text{CH}_2\text{Ph}$, 100)

MS (CI) m/z 175 ($\text{M}^+ + \text{H}$, 83)

HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{O} + \text{H}$: 175.1123, found: m/z 175.1117 (CI, ($\text{M}^+ + \text{H}$), -0.6 mmu)

4-Methyl-3-methylene-1-(toluene-4-sulfonyl)-pyrrolidine (4b)

Reference : Radetich, B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 8007-8008.

Colorless oil (Isolated yield 60%)

IR (neat) 1346, 1165 (sulfonamido peaks) cm^{-1}

^1H NMR (CDCl_3 , 270 MHz) δ 7.71 (d, J = 6.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 4.90 (dd, J = 4.0 and 2.2 Hz, 1H), 4.85 (dd, J = 4.4 and 2.2 Hz, 1H), 3.95 (d, J = 13.9 Hz, 1H), 3.73 (dd, J = 13.9 and 1.8 Hz, 1H), 3.62-3.51 (m, 1H), 2.73-2.67 (m, 2H), 2.44 (s, 3H), 1.04 (d, J = 6.4 Hz, 3H),

^{13}C NMR (CDCl_3 , 67.9 MHz) δ 149.2, 143.5, 132.7, 129.6, 127.7, 105.9, 55.1, 52.2, 37.4, 21.6, 16.1

MS (EI) m/z 251 (M^+ , 58), 236 (M^+ - Me, 17), 155 (Ts, 46), 96 (M^+ - Ts, 100)

HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$: 251.0980, found: m/z 251.0979 (EI, (M^+), -0.1 mmu).

4-Ethyl-2-methyl-3-methylene-2-phenyl-tetrahydrofuran (4c)

Isolated as 3:1 mixture of diastereomers

Colorless oil (Isolated yield 81%)

IR (neat) 1072 (C-O-C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.49 (d, J = 8.9 Hz, major+minor, 2 H), 7.33-7.21 (m, major+minor, 3H), 5.13 (d, J = 2.2 Hz, major, 1H), 5.09 (d, J = 2.7 Hz, minor)*, 5.07 (d, J = 2.5 Hz, major, 1H), 5.05 (d, J = 2.4, minor)*, 4.12 (t, J = 8.2 Hz, major, 1H), 4.01 (t, J = 8.2 Hz, minor)*, 3.62 (dd, J = 8.2 and 6.8 Hz, minor)*, 3.40 (t, J = 8.2 Hz, major, 1H), 2.81-2.72 (m, major, 1H), 2.64-2.55 (m, minor)*, 1.77-1.67 (m, minor)*, 1.62-1.39 (superimposed m, major+minor, 1H), 1.59 (superimposed s, minor)*, 1.58 (superimposed s, major, 3H), 1.27-1.16 (m, major, 1H), 0.94 (t, J = 7.49 Hz, minor)*, 0.81 (t, J = 7.49 Hz, major, 3H)

^{13}C NMR (CDCl_3 , 100.6 MHz) δ 157.79*, 157.66, 145.65*, 145.03, 128.01, 126.72*, 125.39, 124.99*, 106.43, 105.21*, 85.60*, 85.43, 70.12, 69.80*, 46.05, 44.42*, 29.30, 28.06*, 26.48, 25.35*, 12.12, 11.81*

MS (EI) m/z 202 (M^+ , 0.7), 187 (M^+ - Me, 100), 125 (M^+ - Ph, 10)

HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: 202.1358, found: m/z 202.1367 (EI, (M^+), +0.9 mmu)

* Mark corresponds to minor isomer.

A typical experimental procedure of the dehalogenation:

A 10 mL of round bottom flask charged with InCl_3 (0.221 g, 1.0 mmol) was dried by heating at 110 °C under reduced pressure for 1 h. After nitrogen was filled, THF (2 mL) was added to dissolve InCl_3 . NaOMe (1.0 mmol) was added to the mixture and stirred at rt for 0.5 h (When the catalytic amount of InCl_3 was used, stirring time was 1 min). Then Ph_2SiH_2 (2.0 mmol), halide [or haloalkene, or aryl halide and olefin] (1.0 mmol) and 1M Et_3B in hexane (0.1 mL) were added, and the resulting mixture was stirred at rt for 2 h. After deionized water was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over MgSO_4 and concentrated. Purification was performed by column chromatography eluting with hexane/EtOAc. Further purification was performed by TLC eluting with hexane/ Et_2O or distillation under reduced pressure. Product was determined by ^1H NMR.

3-Isopropyl-2,3-dihydro-benzofuran (6a)

Colorless oil (Isolated yield 96%)

IR (neat) 1234 (C-O-C), 1018 cm^{-1}

^1H NMR (CDCl_3 , 270 MHz) δ 7.20-7.10 (m, 2H), 6.88-6.76 (m, 2H), 4.52 (t, J = 9.0 Hz, 1H), 4.38 (dd, J = 5.1 and 9.0 Hz, 1H), 3.36-3.29 (m, 1H), 1.97 (qd, J = 6.8 and 6.6 Hz, 1H), 0.95 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H)

^{13}C NMR (CDCl_3 , 67.9 MHz) δ 18.5, 19.8, 31.7, 48.1, 73.8, 109.3, 120.0, 125.0, 128.1, 129.4, 160.3

MS (EI) m/z 162 (M^+ , 24), 119 (M^+ - CHCH_3CH_3 , 100), 118 (8), 91 (59), 65 (7), 39 (4)

HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: 162.1045, found: m/z 162.1038 (EI, (M^+), -0.7 mmu)

Anal. calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.44; H, 8.70, found: C, 81.15; H, 8.63.

4-Methyl-2-phenyl-tetrahydrofuran (6b)

Reference : Inoue, K.; Sawada, A.; Shibata, I.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 906-907.

Isolated as mixture of diastereomers (*cis:trans* = 2:8)

Colorless oil (Isolated yield 94%)

IR (neat) 1088 (C-O-C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 7.36-7.21 (m, major+minor, 5H), 5.03 (t, J = 7.0 Hz, major, 1H), 4.92 (dd, J = 9.9 and 5.6 Hz, minor)*, 4.22 (dd, J = 8.2 and 7.0 Hz, major, 1H), 4.09 (t, J = 8.0 Hz, minor)*, 3.58 (t, J = 8.0 Hz, minor)*, 3.48 (dd, J = 8.2 and 7.0 Hz, major, 1H), 2.51-2.39 (m, major+minor, 1H), 2.04-1.92 (m, major+minor, 2H), 1.10 (d, J = 6.8 Hz, major+minor, 3H)

^{13}C NMR (CDCl_3 , 100.6 MHz) δ 143.90, 143.38*, 128.27*, 128.22, 127.11*, 126.97, 125.58*, 125.48, 81.56*, 80.04, 75.65, 75.43*, 43.88*, 42.66, 34.94*, 33.18, 17.69, 17.33*

MS (EI) m/z 162 (M^+ , 100), 147 (M^+ - Me, 1), 85 (M^+ - Ph, 3)

HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: 162.1045, found: m/z 162.1045 (EI, (M^+), 0 mmu)

* Mark corresponds to minor isomer (*cis*).

7-Methyl-2,9-dioxabicyclo[4.3.0]nonane (*cis*-6c)

Reference : Beckwith, A. L. J.; Page, D. M. *Tetrahedron* **1999**, *55*, 3245-3254.

Colorless oil (Isolated yield 89%)

IR (neat) 1146 (C-O-C), 1115 (C-O-C) cm^{-1}

^1H NMR (CDCl_3 , 400 MHz) δ 5.28 (d, J = 3.9 Hz, 1H), 3.95 (t, J = 8.0 Hz, 1H), 3.75 (td, J = 10.5 and 3.6 Hz, 1H), 3.66-3.61 (m, 1H), 3.61 (dd, J = 10.0 and 8.0 Hz, 1H), 2.50-2.39 (m, 1H), 1.94-1.87 (m, 1H), 1.71-1.51 (m, 3H), 1.46-1.36 (m, 1H), 0.97 (d, J = 7.0 Hz, 3H)

^{13}C NMR (CDCl_3 , 100.6 MHz) δ 102.16, 71.60, 61.08, 37.73, 35.08, 23.11, 19.36, 11.59

MS (EI) m/z 142 (M^+ , 12), 141 (M^+ - H, 100), 127 (M^+ - Me, 2)

HRMS calcd for $\text{C}_8\text{H}_{14}\text{O}_2 + \text{H}$: 143.1072, found: m/z 143.1073 (CI, ($\text{M}^+ + \text{H}$), +0.1 mmu)

A typical experimental procedure of the intermolecular reaction:

A 10 mL of round bottom flask charged with InCl_3 (0.221 g, 1.0 mmol) was dried by heating at 110 °C under reduced pressure for 1 h. After nitrogen was filled, THF (2 mL) was added to dissolve InCl_3 . NaOMe (1.0 mmol) was added to the mixture and stirred at rt for 0.5 h (When the catalytic amount of InCl_3 was used, stirring time was 1 min). Then Ph_2SiH_2 (2 mmol), alkene (10.0 mmol), halide [or alkyne] and 1M Et_3B in hexane (0.1 mL) were added, and the resulting mixture was stirred at rt for 2 h. After 1N HCl aq was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over MgSO_4 and concentrated. Purification was performed by column chromatography eluting with hexane/EtOAc. Further purification was performed by TLC eluting with hexane/ Et_2O or distillation under reduced pressure. Product was determined by ^1H NMR.

3-Cyclohexyl-2-methyl-propionic acid methyl ester (8b)

Colorless oil (Isolated yield 81%)

IR (neat) 1743 (C=O) cm^{-1}

^1H NMR (CDCl_3 , 270 MHz) δ 3.67 (s, 3H), 2.55 (qt, J = 6.8 and 7.1 Hz, 1H), 1.79-1.50 (m, 6H), 1.32-1.03 (m, 8H), 0.95-0.76 (m, 2H)

^{13}C NMR (CDCl_3 , 67.9 MHz) δ 177.93, 51.42, 41.45, 36.66, 35.28, 33.18, 33.01, 26.43, 26.14, 26.09, 17.43

MS (EI) m/z 184 (M^+ , 4), 153 (M^+ - OMe, 7), 125 (M^+ - COOMe, 8), 101 (M^+ - C_6H_{11} , 49)

HRMS calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2$: 184.1463, found: m/z 184.1459 (EI, M^+), -0.4 mmu)

Anal. calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2$: C, 71.70; H, 10.94, found: C, 71.49; H, 10.66.

2-Methyl-4-phenyl-pent-4-enitrile (10a)

Colorless oil (Isolated yield 44%)

IR (neat) 2241 (CN) cm^{-1}

^1H NMR (CDCl_3 , 270 MHz) δ 7.36-7.30 (m, 5H), 5.41 (s, 1H), 5.23 (s, 1H), 2.95-2.85 (m, 1H), 2.73-2.59 (m, 2H), 1.28 (d, J = 6.8 Hz, 3H)

^{13}C NMR (CDCl_3 , 67.9 MHz) δ 143.8, 139.2, 128.6, 127.9, 126.1, 122.4, 116.2, 40.0, 24.3, 17.6

MS (EI) m/z 171 (M^+ , 73), 117 (M^+ - CHCH_3CN , 100), 103 (M^+ - $\text{CH}_2\text{CHCH}_3\text{CN}$, 19)

HRMS calcd for $\text{C}_{12}\text{H}_{13}\text{N}$: 171.1048, found: m/z 171.1051 (EI, M^+), +0.3 mmu)

2-Methyl-4-phenoxyethyl-pent-4-enitrile (10b)

Colorless oil (Isolated yield 45%)

IR (neat) 2241 (CN), 1242 (Aryl-O-C) cm^{-1}

^1H NMR (CDCl_3 , 270 MHz) δ 7.32-7.25 (m, 2H), 6.99-6.89 (m, 3H), 5.35 (s, 1H), 5.20 (s, 1H), 4.50 (s, 2H), 2.91 (qdd, J = 7.1 and 6.8 and 8.5 Hz, 1H), 2.51 (dd, J = 14.7 and 8.5 Hz, 1H), 2.41 (dd, J = 14.7 and 6.8 Hz, 1H), 1.36 (d, J = 7.1 Hz, 3H)

^{13}C NMR (CDCl_3 , 67.9 MHz) δ 158.2, 140.1, 129.5, 122.5, 121.1, 116.8, 114.6, 70.5, 37.8, 24.4, 18.0

MS (EI) m/z 201 (M^+ , 69), 186 (M^+ - Me, 17), 172 (10), 158 (18), 147 (M^+ - CHCH_3CN , 82), 133 (M^+ - $\text{CH}_2\text{CHCH}_3\text{CN}$, 25), 118 (16), 108 (M^+ - OPh, 100), 94 (M^+ - CH_2OPh , 69), 93 (44), 81 (82), 77 (43)

HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$: 201.1154, found: m/z 201.1157 (EI, (M^+), +0.3 mmu)

Anal. calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$: C, 77.58; H, 7.51; N, 6.96, found: C, 77.66; H, 7.39; N, 7.04.

4a

^1H NMR spectrum

^{13}C NMR spectrum

4b

^1H NMR spectrum

^{13}C NMR spectrum

3:1 mixture of diastereomers

^1H NMR spectrum

^{13}C NMR spectrum

6a

^1H NMR spectrum

^{13}C NMR spectrum

mixture of diastereomers (*cis:trans* = 2:8)

¹H NMR spectrum

¹³C NMR spectrum

6c (cis)

^1H NMR spectrum

^{13}C NMR spectrum

^1H NMR spectrum

^{13}C NMR spectrum

¹H NMR spectrum

¹³C NMR spectrum

^1H NMR spectrum

^{13}C NMR spectrum