Synthesis of Biaryls via Unusual Deoxygenative Dimerization of 1,4-Epoxy-1,4-dihydroarenes Catalyzed by Palladium Complexes

Huai-Ting Shih, Hung-Hsin Shih and Chien-Hong Cheng *

Department of Chemistry, Tsing Hua University, Hsinchu, Taiwan 300

chcheng@mx.nthu.edu.tw

Supporting Information

Synthesis of Compound 2a from 1,4-Dihydro-1,4-epoxylnaphthalene and Trichlorosilane.

A two-necked flask equipped with a magnetic stir bar was charged with 1,4-dihydro-1,4-epoxylnaphthalene (0.144 g, 1.00 mmol) and $Pd(dba)_2$ (0.014 g, 0.025 mmol). The flask under 1 atm. of nitrogen was added toluene (2 mL) via a syringe. The mixture was stirred at room temperature for 3 minutes. After the color of mixture changed from purple to light yellow, the system was cooled in a ice-water bath. Trichlorosilane (0.25 mL, 2.5 mmol) was injected dropwise into the mixture in ca. 0.5 min. The flask was then removed from the ice-water bath and stirred at room temperature for 1 minute. The solution was filtered through a silica gel/Celite pad and was washed with 80 mL of CH_2Cl_2. The combined filtrate was concentrated on a rotary evaporator. Separation of the residue on a silica gel column using a mixture of hexane and ethyl acetate as eluent gave **2a** (0.122 g) in 94 % yield.

Similar procedures were employed for the preparation of products **2f**, **3b** and **3c**.

Synthesis of Compound 3a from 1,4-Dihydro-1,4-epoxylnaphthalene and Trichlorosilane.

A two-necked flask equipped with a magnetic stir bar was charged with **1a** (0.144 g, 1.00 mmol), Zn podwer (0.131 g, 2.00 mmol) and $Pd(dba)_2$ (0.014 g, 0.025 mmol). To the flask under 1 atm. of nitrogen was added toluene (2 mL) via a syringe. The mixture was stirred at room temperature for 3 min. After the color of mixture changed from purple to light yellow, the mixture was cooled by ice-water bath. Trichlorosilane(0.25 mL, 2.5 mmol) was injected dropwise into the mixture in ca. 0.5 min. The flask was then removed from the ice-water bath and stirred at room temperature for 6 h. The solution was filtered through a silica gel/Celite pad and was washed with 80 mL of CH_2Cl_2. The combined filtrate was concentrated on a rotary evaporator. Separation of

the residue on a silica gel column using a mixture of hexane and ethyl acetate as eluent gave **3a** (0.124 g) in 98 % yield.

Other products **3d, 3e**, **3g** and **3h** were prepared similarly. The detailed reaction conditions were listed in Table 2. The spectral data of these products were shown below.

9-(2-Naphthyl)-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene (2a). Mp.: 106℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.82 (m, 4 H), 7.61-7.59 (m, 1 H), 7.50-7.45 (m, 2 H), 7.34-7.32 (m, 2 H), 7.26-7.23 (m, 2 H), 5.62 (d, J = 4.4 Hz, 1 H), 5.37 (s, 1 H), 3.07 (dd, J = 8.4, 4.4 Hz, 1 H), 2.22-2.11 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.10, 145.98, 142.46, 133.53, 132.28, 128.25, 127.62, 127.56, 126.70, 126.63, 126.17, 125.98, 125.83, 125.34, 119.16, 118.34, 85.28, 79.24, 46.03, 38.36. HRMS (FAB$^+$): calcd for ($C_{20}H_{16}O$): 272.1201. Found: ([M]$^+$) 272.1211.

2,2'-Binaphthyl (3a). Mp.: 178℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18(d, J = 1.2 Hz, 2 H), 7.98-7.78(m, 8 H), 7.54-7.48(m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.38, 133.71, 132.64, 128.49, 128.21, 127.65, 126.33, 126.09, 125.98, 125.71. HRMS (FAB$^+$): calcd for ($C_{20}H_{15}$): 255.1174. Found: ([M+H]$^+$) 255.1176.

1-Methyl-3-(4-methyl-2-naphthyl)naphthalene (3b). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.02 (m, 4 H), 7.96-7.93 (m, 2 H), 7.43 (s, 2 H), 7.55-7.53 (m, 4 H), 2.80 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.11, 134.85, 133.94, 131.89, 128.84, 126.44, 126.00, 125.78, 124.46, 124.01, 19.51. HRMS (FAB$^+$): calcd for ($C_{22}H_{18}$): 282.1409. Found: ([M]$^+$) 282.1404.

1-Methyl-2-(4-methyl-2-naphthyl)naphthalene (3b'). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.12 (m, 2 H), 7.94-7.90 (m, 2 H), 7.81-7.76 (m, 1 H), 7.72 (s, 1 H), 7.62-7.59 (m, 4 H), 7.41 (s, 1 H), 2.79 (s, 3 H), 2.68 (s, 3 H). HRMS (FAB$^+$): calcd for ($C_{22}H_{18}$): 282.1409. Found: ([M]$^+$) 282.1404.

2-(1,4-Dimethyl-2-naphthyl)-1,4-dimethylnaphthalene (3c). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.07 (m, 4 H), 7.60-7.57 (m, 4 H),, 7.20 (s, 2 H), 2.71 (s, 6 H), 2.42 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.98, 132.92, 131.97, 131.60, 129.55, 128.92, 125.75, 125.16, 124.97, 124.64, 19.29, 15.72. HRMS (FAB^+): calcd for ($C_{24}H_{22}$): 310.1721. Found: ($[M]^+$) 310.1715.

6-(6,7-Dimethoxy-2-naphthyl)-2,3-dimethoxynaphthalene (3d). Mp.: 281℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 1.2 Hz, 2 H), 7.79 (d, J = 8.4 Hz, 2 H), 7.72 (dd, J = 8.4, 1.2 Hz, 2 H), 7.21 (s, 2 H), 7.17 (s, 2 H), 4.03 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.10, 149.82, 137.40, 129.79, 128.54, 127.04, 124.61, 124.22, 106.86, 106.40, 56.10. HRMS (EI^+): calcd for ($C_{24}H_{22}O_4$): 374.1518. Found: ($[M]^+$) 374.1517.

6-Naphtho[2,3-*d*][1,3]dioxol-6-ylnaphtho[2,3-*d*][1,3]dioxole (3e). Mp.: 265℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 2 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.68 (dd, J = 8.4 Hz, 1.6 Hz, 2 H), 7.19 (s, 2 H), 7.15 (s, 2 H), 6.06 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.94, 147.65, 137.13, 130.85, 129.62, 127.46, 125.07, 124.06, 104.10, 103.68, 101.03. HRMS (EI^+): calcd for ($C_{22}H_{14}O_4$): 342.0892. Found: ($[M]^+$) 342.0865.

4,5-Dibromo-9-(6,7-dibromo-2-naphthyl)-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7), 3,5-triene (2f). Mp.: 242℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1 H), 8.10 (s, 1 H), 7.72-7.55 (m, 5 H), 5.55 (d, J = 3.6 Hz, 1 H), 5.28 (s, 1 H), 3.02 (dd, J = 7.8 , 5.4 Hz, 1 H), 2.14 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.00, 146.63, 143.19, 133.17, 132.01, 131.96, 127.45, 127.36, 124.90, 124.73, 124.43, 122.86, 122.68, 122.31, 121.60, 84.53, 78.75, 45.72, 38.04. HRMS (FAB^+): calcd for ($C_{20}H_{12}$ $^{79}Br_2$ $^{81}Br_2O$): 587.7581. Found: ($[M]^+$) 587.7549.

7-(3-Phenanthryl)-1,4-dihydrophenanthrene (3g'). Mp.: 180℃. ^{1}H NMR (400

MHz, $CDCl_3$): δ 8.82 (d, J = 8.4 Hz, 2 H), 8.75 (d, J = 8 Hz, 2 H), 8.29 (d, J = 2 Hz, 2 H), 8.10 (dd, J = 8.4, 2 Hz, 2 H), 7.93 (d, J = 7.6 Hz, 2 H), 7.87 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 9.2 Hz, 2 H), 7.70-7.61 (m, 4 H). HRMS (EI^+): calcd for ($C_{28}H_{18}$): 354.1408. Found: ($[M]^+$) 354.1410.

2-(5,8,9,12-Tetrahydro-2-triphenylenyl)triphenylene (3h). Mp.: 356℃. ^1H NMR (400 MHz, $CDCl_3$): δ 9.06 (d, J = 2 Hz, 2 H), 8.87-8.81 (m, 4 H), 8.75-8.70 (m, 6 H), 8.12 (dd, J = 1.6, 8.4 Hz, 2 H), 7.74-7.70 (m, 8 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.88, 130.25, 130.12, 129.88, 129.81, 129.64, 129.12, 127.47, 127.38, 127.35, 126.62, 124.08, 123.45, 123.43, 123.40, 122.08. HRMS (EI^+): calcd for ($C_{36}H_{22}$): 454.1722. Found: ($[M]^+$) 454.1722.