

## **Novel Cyclization Reaction of 1, $\omega$ -Diiodo-1-alkynes without the Loss of Iodine Atoms**

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**5-Ethoxy-3-diiodomethylene-2,2-dimethyltetrahydrofuran (2a) (Typical Procedure for Cycloisomerization of Diiodoalkynes 1).** To a solution of 1-hexyne (23  $\mu$ L, 0.20 mmol) in THF (2 mL) under argon atmosphere at 0 °C was added *n*-BuLi (1.6 M solution in hexane, 0.14 mL, 0.22 mmol). The resulting solution was stirred at 0 °C for 30 min. To the resulting solution of 1-hexynyllithium in THF was added diiodoalkyne **1a** (0.408 g, 1.0 mmol). The resulting solution was stirred at 40 °C for 2 h. The mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were dried (MgSO<sub>4</sub>) and concentrated in *vacuo*. The residue was purified by flash chromatography (SiO<sub>2</sub>, 2–5% ethyl acetate in hexane) to afford 0.346 g (85% yield) of **2a**: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.11 (3H, t, *J* = 7.0 Hz), 1.54 (1H, s), 1.71 (1H, s), 2.62 (1H, dd, *J* = 5.5 and 17.4 Hz), 2.88 (1H, d, *J* = 17.4 Hz), 3.24 (1H, m), 3.75 (1H, m), 4.76 (1H, d, *J* = 5.4 Hz); <sup>13</sup>C NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  –2.6, 15.2, 26.7, 27.0, 52.5, 62.4, 85.2, 99.0, 161.3.

**3-Diiodomethylene-2,2-dimethyltetrahydrofuran (2b):** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.47 (6H, s), 2.75 (2H, t, *J* = 8.3 Hz), 3.81 (2H, t, *J* = 8.3 Hz); <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>)  $\delta$  –3.6, 24.2, 45.9, 61.8, 84.3, 162.4. Anal. Calcd for C<sub>7</sub>H<sub>10</sub>OI<sub>2</sub>: C, 23.10; H, 2.77. Found: C, 23.53; H, 2.76.

**4-Diiodomethylene-2-ethoxy-1-oxaspiro[4.5]decane (2c):** <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.11 (3H, t, *J* = 7.1 Hz), 1.31 (1H, m), 1.52 (1H, br d, *J* = *ca.* 13 Hz), 1.68 (3H, m), 1.82–2.01 (3H, m), 2.41–2.52 (2H, m), 2.64 (1H, dd, *J* = 5.4 and 17.2 Hz), 2.91 (1H, d, *J* = 17.2 Hz), 3.27 (1H, m), 3.76 (1H, m), 4.77 (1H, d, *J* = 5.4 Hz); <sup>13</sup>C NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  –2.7, 14.9, 22.3, 22.6, 25.2, 33.4, 34.0, 52.7, 62.2, 86.6, 98.7, 159.7.

**4-Diiodomethylene-1-oxaspiro[4.5]decane (2d):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (1H, m), 1.22 (2H, m), 1.50–1.70 (5H, m), 2.24 (2H, m), 2.73 (2H, t,  $J = 6.9$  Hz), 3.76 (2H, t,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  -3.8, 21.9, 24.9, 30.8, 46.6, 61.8, 85.8, 161.3.

**3-Diiodomethylene-2-isobutyl-2-methyltetrahydrofuran (2e):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.93 (3H, d,  $J = 6.5$  Hz), 0.94 (3H, d,  $J = 6.5$  Hz), 1.39 (3H, s), 1.51 (1H, dd,  $J = 6.7$  and 14.8 Hz), 1.74 (1H, sept,  $J = 6.5$  Hz), 2.01 (1H, dd,  $J = 5.5$  and 14.8 Hz), 2.65–2.79 (2H, m), 3.76 (1H, dt,  $J = 7.0$  and 8.6 Hz), 3.82 (1H, dt,  $J = 4.6$  and 8.1 Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  3.1, 23.0, 23.9, 24.3, 24.6, 44.8, 46.6, 61.6, 87.1, 161.8. Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{OI}_2$ : C, 29.58; H, 3.97. Found: C, 29.75; H, 3.70.

**5-Ethoxy-3-diiodomethylene-2-(2-phenylethyl)tetrahydrofuran (2f):** One diastereomer;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.13 (3H, t,  $J = 7.1$  Hz), 1.90–2.02 (1H, m), 2.26–2.43 (3H, m), 2.75 (1H, d), 2.77–2.88 (2H, m), 3.31 (1H, m), 3.78 (1H, m), 4.59 (1H, dt,  $J = 2.2$  and 8.1 Hz), 5.10 (1H, d,  $J = 5.0$  Hz), 7.16–7.31 (5H, m). Another diastereomer;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.15 (3H, t,  $J = 7.1$  Hz), 2.08–2.19 (1H, m), 2.31–2.39 (1H, m), 2.50 (1H, d,  $J = 5.7$  Hz), 2.60 (1H, dt,  $J = 1.9$  and 18.2 Hz), 2.78–3.01 (2H, m), 3.30 (1H, m), 3.84 (1H, m), 4.45 (br d,  $J = 11.0$  Hz), 5.05 (1H, dd,  $J = 1.9$  and 5.8 Hz), 7.18–7.32 (5H, m).

**3-Diiodomethylene-2-(2-phenylethyl)tetrahydrofuran (2g):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.88 (1H, m), 2.11 (1H, m), 2.60–2.63 (2H, m), 2.70 (1H, ddd,  $J = 7.0, 9.7$ , and 13.7 Hz), 2.81 (1H, m), 4.06 (1H, m), 4.16 (1H, m), 4.32 (1H, br d,  $J = 9.5$  Hz), 7.18–8.31 (5H, m);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  -1.0, 31.6, 32.7, 41.5, 66.1, 84.3, 125.9, 128.4, 128.6, 141.4, 160.0.

**3-Diiodomethylene-2-(2-phenylethyl)tetrahydropyran (2h):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.65–1.82 (3H, m), 2.08–2.23 (2H, m), 2.69 (1H, ddd,  $J = 2.3, 6.6$ , and 13.8 Hz), 2.80–2.87 (2H, m), 3.53 (1H, td,  $J = 4.3$  and 11.5 Hz), 3.75 (1H, m), 4.58 (1H, dd,  $J = 3.7$  and 10.5 Hz), 7.16–7.33 (5H, m);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  11.0, 25.9, 31.3, 31.7, 33.5, 60.0, 80.9, 125.9, 128.4, 128.6, 141.4, 152.3.

**2-Cyclohexyl-3-diiodomethylenetetrahydropyran (2i):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.04 (1H, m), 1.12–1.24 (4H, m), 1.41 (1H, m), 1.63–1.84 (5H, m), 1.97 (2H, m), 2.16 (1H, dt,  $J = 6.0$  and 13.7 Hz), 2.86 (1H, br d,  $J = ca. 15$  Hz), 3.49 (1H, m), 3.74 (1H, dt,  $J = 4.1$  and 11.2 Hz), 4.32 (1H, d,  $J = 9.6$  Hz);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  12.3, 25.9, 26.3, 26.4, 27.4, 28.5, 29.2, 34.2, 37.3, 59.9, 85.1, 152.4.

**Diiodomethylenecyclopentane (2j):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.89 (4H, m), 2.29 (4H, m);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  0.6, 27.8, 41.0, 162.7. Anal. Calcd for  $\text{C}_6\text{H}_8\text{I}_2$ : C, 21.58; H, 2.41. Found: C, 21.31; H, 2.31.

**[2-(2-Diiodomethylenecyclopentyl)ethyl]benzene (2k):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.53 (1H, m), 1.85–2.02 (5H, m), 2.27 (1H, m), 2.39 (1H, m), 2.58–2.66 (2H, m), 2.72 (1H, ddd,  $J = 4.9, 10.5,$  and  $15.1$  Hz), 7.17–7.33 (5H, m);  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CDCl}_3$ )  $\delta$  1.4, 24.7, 31.6, 33.4, 34.1, 40.4, 50.4, 125.8, 128.3, 128.5, 141.8, 165.4.