Electronic Supplementary Information for

Novel Cyclization Reaction of 1,ω-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 μL, 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 (MgSO4) and concentrated in vacuo. The residue was purified by flash chromatography (SiO2, 2–5% ethyl acetate in hexane) to afford 0.346 g (85% yield) of 2a: 1H NMR (500 MHz, C6D6) δ 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); 13C NMR (125.8 MHz, C6D6) δ –2.6, 15.2, 26.7, 27.0, 52.5, 62.4, 85.2, 99.0, 161.3.

3-Diiodomethylene-2,2-dimethyltetrahydrofuran (2b): 1H NMR (500 MHz, CDCl3) δ 1.47 (6H, s), 2.75 (2H, t, J = 8.3 Hz), 3.81 (2H, t, J = 8.3 Hz); 13C NMR (125.8 MHz, CDCl3) δ –3.6, 24.2, 45.9, 61.8, 84.3, 162.4. Anal. Calcd for C7H10OI2: C, 23.10; H, 2.77. Found: C, 23.53; H, 2.76.

4-Diiodomethylene-2-ethoxy-1-oxaspiro[4.5]decane (2c): 1H NMR (500 MHz, C6D6) δ 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); 13C NMR (125.8 MHz, C6D6) δ –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]decanes (2d): ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125.8 MHz, CDCl₃) δ –3.8, 21.9, 24.9, 30.8, 46.6, 61.8, 85.8, 161.3.

3-Diiodomethylene-2-isobutyl-2-methyltetrahydrofuran (2e): ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125.8 MHz, CDCl₃) δ 3.1, 23.0, 23.9, 24.3, 24.6, 44.8, 46.6, 61.6, 87.1, 161.8. Anal. Calcd for C₁₀H₁₆OI₂: C, 29.58; H, 3.97. Found: C, 29.75; H, 3.70.

5-Ethoxy-3-diiodomethylene-2-(2-phenylethyl)tetrahydrofuran (2f): One diastereomer; ¹H NMR (300 MHz, C₆D₆) δ 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; ¹H NMR (300 MHz, C₆D₆) δ 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)tetrahydropyran (2h): ¹H NMR (500 MHz, CDCl₃) δ 1.65–1.82 (3H, m), 2.08–2.23 (2H, m), 2.69 (1H, dd, 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); ¹³C NMR (125.8 MHz, CDCl₃) δ 11.0, 25.9, 31.3, 31.7, 33.5, 60.0, 80.9, 125.9, 128.4, 141.4, 152.3.

2-Cyclohexyl-3-diiodomethylenetetrahydropyran (2i): ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125.8 MHz, CDCl₃) δ 12.3, 25.9, 26.3, 26.4, 27.4, 28.5, 29.2, 34.2, 37.3, 59.9, 85.1, 152.4.

Diiodomethylene cyclopentane (2j): ¹H NMR (500 MHz, CDCl₃) δ 1.89 (4H, m), 2.29 (4H, m); ¹³C NMR (125.8 MHz, CDCl₃) δ 0.6, 27.8, 41.0, 162.7. Anal. Calcd for C₆H₁₂I₂: C, 21.58; H, 2.41. Found: C, 21.31; H, 2.31.
[2-(2-Diiodomethylene)cyclopentyl]ethyl]benzene (2k): $^{1}$H NMR (500 MHz, 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); $^{13}$C NMR (125.8 MHz, 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.