

Supplementary Information

Double Carbonylation of Zirconocene-Alkyne Complexes

Shizue Mito and Tamotsu Takahashi*

Experimental

All reactions were carried out under dry nitrogen. THF was distilled over sodium and benzophenone. Zirconocene dichloride was obtained from NICHIA Corporation. Alkynes and phosphines were purchased from TCI Co. Ltd. or Aldrich Chemical Co., Inc. *n*-Butyllithium (1.6 M in *n*-hexane) was purchased from Kanto Chemical. Co. Ltd. Column chromatography was performed on silica gel (Kanto Chemical. 60 mesh). Alkynes that are commercially available were prepared by a known procedure.¹

¹H and ¹³C NMR spectra were recorded for CDCl₃ (contain 0.3 % Me₄Si) solution at 25 °C on a Bruker-400 or JEOL-AL300 NMR spectrometer. GC analysis was performed on a Shimadzu GC-14A instrument equipped with a Shimadzu CBP1-M25-O25 fused silica capillary column and Shimadzu C-R6A-Chromatopac integrator. GC yields were determined using dodecane as an internal standard.

General Procedure for the Reaction of Zirconocene-Alkyne Complexes with CO.

2,3-Dihexyl-4hydroxycyclobut-2-enone (2a)

A 20 mL Schlenk tube under dried nitrogen was charged with Cp₂ZrCl₂ (350 mg, 1.2 mmol) and THF (5 mL). The mixture was cooled to -78°C (dry ice/acetone bath), and then 1.56 M *n*-BuLi in *n*-hexane (1.53 mL, 2.4 mmol) was added dropwise via a syringe. The reaction mixture was stirred at -78 °C for 1 h. 1.0 M Trtrimethylphosphine in THF (1.20 mL, 1.2 mmol) was added, and then the reaction mixture was gradually warmed to room temperature and was stirred for 1 h. 7-Tetradecyne (194 mg, 1.0 mmol) was added, and then the reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was cooled down to 0 °C. Carbon monoxide was slowly introduced in the mixture by bubbling and the mixture was stirred for 6 h. The reaction mixture was quenched with 3N HCl aq., and extracted with diethyl ether twice. The extract was then washed with brine and dried over MgSO₄. The solvent was evaporated in vacuo. Column chromatography on silica gel (5/1 hexane/AcOEt) afforded the product as a pale yellow oil. GC yield 65 %. Isolated yield 48 %. IR (neat): ν 3395 (OH), 1711(C=O) cm⁻¹; ¹H

NMR (CDCl₃, Me₄Si) δ 0.85-0.92 (m, 6H), 1.26-1.40 (m, 12H), 1.46-1.73 (m, 4H), 2.09-2.15 (m, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 3.66 (br, 1H), 5.10 (s, 1H). ¹³C NMR (CDCl₃, Me₄Si) δ 13.98, 22.47, 23.30, 26.12, 26.85, 27.50, 28.05, 29.15, 29.40, 31.40, 31.43, 84.00, 151.85, 179.78, 194.18. HRMS calcd for C₁₆H₂₈O₂ 252.2089, found 252.2108.

4-Deutrio-2,3-Dihexyl-4-hydroxycyclobut-2-enone (2a-D)

The reaction of zirconocene-7-tetradecyne complex and CO using trimethylphosphine as described above gave the title compound **2a-D** as a pale yellow oil after quench with 20% DCl in D₂O instead of 3N HCl aq. GC yield 58 %. Isolated yield 20 %. ¹H NMR (CDCl₃, Me₄Si) δ 0.85-0.91 (m, 6H), 1.23-1.41 (m, 12H), 1.45-1.72 (m, 4H), 2.09-2.14 (m, 2H), 2.57 (td, *J* = 7.6, 3.0 Hz, 2H). ¹³C NMR (CDCl₃, CHCl₃) δ 14.03, 22.50, 23.35, 26.18, 26.88, 27.48, 29.18, 29.42, 29.68, 31.42, 31.46, 152.26, 179.26, 193.50. HRMS calcd for C₁₆H₂₆D₂O₂ 254.2213, found 254.2202.

2,3-Dibutyl-4-hydroxycyclobut-2-enone (2b)

The reaction of zirconocene-5-decyne complex using dimethylphenylphosphine and CO at -15 °C as described above gave the title compound **2b** as a pale yellow oil. GC yield 38 %. Isolated yield 24 %. ¹H NMR (CDCl₃, Me₄Si) δ 0.88-0.98 (m, 6H), 1.25-1.75 (m, 8H), 2.13 (td, *J* = 7.2, 3.3 Hz, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 3.40 (bs, 1H), 5.09 (s, 1H). ¹³C NMR (CDCl₃, CHCl₃) δ 13.63, 13.69, 22.56, 22.84, 23.03, 27.21, 28.28, 28.99, 84.23, 151.97, 179.53, 193.81. HRMS calcd for C₁₂H₂₀O₂ 196.1463, found 194.1464.

2,3-Didecyl-4-hydroxycyclobut-2-enone (2c)

The reaction of zirconocene-11-dodecyne complex using dimethylphenylphosphine and CO at -15 °C as described above gave the title compound **2c** as a pale yellow oil. GC yield 26 %. Isolated yield 13 %. ¹H NMR (CDCl₃, Me₄Si) δ 0.79-0.83 (m, 6H), 1.14-1.67 (m, 32H), 2.05 (td, *J* = 7.5, 3.3 Hz, 2H), 2.50 (t, *J* = 7.5 Hz, 2H), 3.12 (bs, 1H), 5.02 (s, 1H). ¹³C NMR (CDCl₃, CHCl₃) δ 14.05, 22.66, 23.35, 26.23, 26.92, 27.51, 29.25, 29.29, 29.50, 29.54, 29.56, 29.78, 31.87, 84.29, 152.09, 179.44, 193.65. HRMS calcd for C₂₄H₄₄O₂ 364.3341, found 364.3349.

Reference

1. P. J. Garratt: *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and G. Pattenden, ERS, Pergamon Press, 1991, Vol. 3, p. 271.