1,1-Cycloaddition of Oxalyl Dichloride with Dialkenylmetal Compounds: Formation of Cyclopentadienone Derivatives by the Reaction of 1,4,- Dilithio-1,3-dienes or Zirconacyclopentadienes with Oxalyl Chloride in the presence of CuCl

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Procedure of the reaction of dilithiodiene with oxalyl chloride: Dilithio compound **1a** was prepared *in situ* from 475 mg (1.0 mmol) 1-iodo-2- [1-(iodo-phenyl-methylene)-pentyl]-benzene and 2.7 mL (4.0 mmol) of a *t*-butyllithium/hexane solution (1.5 M) at -78°C. 196 mg of CuCl (2.0 mmol) was introduced before 1.2 mmol oxalyl chloride was added to the solution (caution: much gas was emitted from the reaction system!). Kept the reaction mixture for 30 minutes, then the mixture was quenched with 3N HCl and extracted with 20ml ether in 3 times. The extract was washed with NaHCO₃ and brine, and dried over MgSO₄. The solvent was evaporated in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether/ CH₂Cl₂=3:1 as elution) to afford **3a**¹ as orange oil (178mg, 68% isolated yield). IR (neat): 1706, 1716 cm⁻¹ (C=O). ¹H NMR (C₆D₆, Me₄Si) δ 0.93 (t, 3H, *J* = 7.2 Hz), 1.43-1.48 (m, 2H), 1.1.66-1.72 (m, 2H); 2.70 (t, 2H, *J* = 7.5 Hz), 7.18-7.51 (m, 9H); ¹³C

NMR (C_6D_6 , Me_4Si) δ 13.78, 23.03, 26.50, 30.28, 119.89, 122.31, 127.69, 128.28, 128.70, 129.34, 130.73, 133.30, 133.50, 145.15, 158.87, 196.76. HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{O}$ 262.1358, found 262.1362.

3b: Orange oil in 82% isolated yield (251mg, GC yield 94%). IR (neat): 1716 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR, ^{13}C NMR data are consistent with the published data.⁴

3c: Deep red viscous oil. Isolated yield 49% (156mg). IR (neat): $1709, 1696\text{ cm}^{-1}$ ($\text{C}=\text{O}$). ^1H NMR, ^{13}C NMR data are consistent with the published data.⁴

Typical procedure of the reaction of zirconacyclopentadiene with oxalyl chloride: To a THF solution of zirconacyclopentadiene **4d**, prepared *in situ* from 2.0mmol diphenylacetylene and 1.0mmol “ Cp_2Zr ” by reported procedures,² 2.0mmol CuCl and 2.0mmol DMPU were added at 0°C . After addition of 1.5mmol oxalyl chloride, much gas was generated from the reaction system. Kept the reaction mixture for 30 minutes at 0°C , then the mixture was quenched with 3N HCl and extracted with 20ml ether in 3 times. The extract was washed with NaHCO_3 and brine, and dried over MgSO_4 . The solvent was evaporated in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether/ Et_2O =50:1 as elution) to afford **3d**³ as dark red solid (256mg, 67% isolated yield). IR (neat): 1716 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR (C_6D_6 , Me_4Si) δ 6.92-7.23 (m); ^{13}C NMR (C_6D_6 , Me_4Si) δ 125.32, 127.44, 128.00, 128.47, 129.32, 130.14, 130.77, 133.10, 154.47, 200.28. HRMS calcd for $\text{C}_{29}\text{H}_{20}\text{O}$ 384.1514, found 384.1520.

3e: Orange liquid in 87% isolated yield (216 mg, GC yield 96%). IR (neat): 1716 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR, ^{13}C NMR data are consistent with the published data.⁴

3f⁵: Reddish oil. Isolated yield 50% (140mg), IR (neat): 1712 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR (CDCl_3 , Me_4Si) δ 1.26 (t, $J = 6.0\text{ Hz}$, 4H), 1.55 (t, $J = 6.0\text{ Hz}$, 4H), 7.23-7.33 (m, 10H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 17.22, 22.70, 128.24, 128.44, 130.04, 135.33, 138.38, 141.19, 198.35; HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{O}$, 286.1358, found 286.1354.

3g: Orange oil. Isolated yield 50% (138mg, GC yield 71%). IR (neat): 1716 cm^{-1} (C=O). ^1H NMR(CDCl_3 , Me_4Si) δ 0.86-1.02 (m, 14H), 1.26-1.54 (m, 12H), 2.09-2.09 (m, 2H), 2.21-2.26 (m, 2H), 2.60-2.67 (m, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.92, 13.95, 14.28, 14.43, 22.55, 22.63, 22.87, 22.95, 23.32, 23.46, 24.94, 26.50, 31.28, 31.87, 122.04, 125.80, 135.86, 155.00, 204.90; HRMS calcd for $\text{C}_{19}\text{H}_{32}\text{O}$, 276.2453, found 276.2448

Procedure for the reaction of zirconacyclopentadiene with oxalyl chloride in the absence of DMPU. Formation of Compound 5. To a THF solution of zirconacyclopentadiene **4e**, 2.0mmol CuCl was added at 0°C . After addition of 2.0mmol oxalyl chloride, the reaction mixture was heated to 50°C and kept for **3h**. Then the mixture was quenched with 3N HCl and extracted with 20ml ether in 3 times. The extract was washed with NaHCO_3 and brine, and dried over MgSO_4 . The solvent was evaporated in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether/ Et_2O =50:1 as elution) to afford the product **5** as orange oil in 69% isolated yield (170mg, GC yield 78%). IR (neat): 1698 cm^{-1} (C=O). ^1H NMR (C_6D_6 , Me_4Si) δ 0.82-1.17 (m, 12H), 1.40-1.67 (m, 8H), 1.84-1.85 (m, 2H), 2.16-2.23 (m, 4H); 2.45 (t, 1H, J = 4.5 Hz), 5.67(t, 1H, J = 6.6 Hz); ^{13}C NMR (C_6D_6 , Me_4Si) δ 14.08, 14.31, 14.44, 14.53, 17.72, 21.74, 22.78, 22.89, 25.68, 28.61, 32.88, 46.49, 126.24, 139.79, 141.54, 167.24, 208.61. HRMS calcd for $\text{C}_{17}\text{H}_{28}\text{O}$ 248.2140, found 248.2145.

Representative procedure for the synthesis of Oxalic acid 1-methoxycarbonyl-2,3,4,5-tetrapropyl-cyclopenta-2,4-dienyl ester methyl ester 11. To a solution of Cp_2ZrCl_2 (1.20mmol, 0.352g) in THF (5.0ml) was added $n\text{-BuLi}$ (1.6M in hexane, 2.4mmol) at -78°C and the mixture was stirred for 1h. After addition of 4-octyne (2.0mmol, 288 μL), the mixture was warmed up to 0°C and stirred for 1h. After CuCl (2.0mmol, 200mg) and methyl chlorooxoacetate (90 μL , 1.0mmol) added, the reaction mixture was warmed to 50°C for 3h. After normal work-up, the product was purified by column chromatography with hexane / methylene dichloride =1:2 as elution to afford the titled compound as a yellow liquid (90mg, 46%). ^1H NMR (CDCl_3 , Me_4Si) δ 0.76-0.87 (m, 12H), 1.21-1.41 (m, 8H), 1.98-2.14 (m, 8H), 3.55 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.16, 14.43, 21.99,

22.47, 27.84, 27.91, 52.28, 53.53, 94.02, 135.53, 146.33, 154.49, 157.76, 168.85. HRMS: $C_{22}H_{34}O_6$, 394.2355, found 394.2351.

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