Supporting Information for

Acyl-lithiation of Olefins: Formation of Cyclopentenones from 1-Lithio-butadienes and CO

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General

All reactions were conducted under a slightly positive pressure of dry, pre-purified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran (THF) and diethyl ether were refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. *t*-BuLi was obtained from Kanto Chemicals Co. Ltd.

NMR spectra were recorded on a JEOL-AL300 NMR spectrometer using CDCl₃ as the solvent with TMS as an internal standard. 1-Iodo-1,3-butadiene derivatives were synthesized by the reported procedure.¹

A typical procedure for the preparation of 3-cyclopentenone derivative **2a from the corresponding 1-lithio-butadienes **1a**.**

To a THF-Et₂O (5ml, 1:1) solution of 1-iodo-1,2,3,4-tetrapropyl-1,3-butadiene (1.0 mmol) at -78 °C was added *t*BuLi (2.0 mmol, 1.47 M in pentane). After this reaction mixture was stirred at -78 °C for 1h, CO gas was introduced from a CO cylinder and was bubbled for 10 min at -78 °C. The reaction mixture was then stirred under a slightly positive pressure of CO for 1h. Hydrolysis of the reaction mixture with aqueous NH₄Cl and followed by normal workup afforded 2,3,4,5-tetrapropyl-3-cyclopentenone **2a** as a mixture of cis and trans isomers in a ratio of 4:1 in 93% combined isolated yield (233mg). Colorless liquid. ¹H NMR (CDCl₃) for the main product: δ 0.73-0.85 (m, 12H), 1.10-1.16 (m, 12H), 1.77-1.96 (m, 2H), 2.10-2.29 (m, 2H), 2.70 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (CDCl₃) for the main product: δ 13.98, 14.16, 19.54, 21.05, 28.22, 30.92, 52.79, 136.36, 221.68. HRMS calcd for C₁₇H₃₀O 250.2297, found 250.2230.

Deuteriolysis of the above reaction mixture with D₂O instead of hydrolysis afforded monodeuterated 3-cyclopentenone **2aD** as a mixture of cis and trans isomers in a ratio of 4:1 in 91% combined isolated yield (228mg) with more than 95% of deuterium incorporation.^{2,3} ¹H

NMR (CDCl₃) for the main product: δ 0.71-0.83 (m, 12H), 0.96-1.59 (m, 12H), 1.75-1.92 (m, 2H), 2.08-2.23 (m, 2H), 2.68 (t, J = 6.0 Hz, 1H). ¹³C NMR (CDCl₃) for the main product: δ 14.15 (2CH₃), 14.35 (2CH₃), 19.64, 19.67, 21.16 (2CH₂), 28.32 (2CH₂), 31.00, 31.08, 52.53 (t, J = 19.1 Hz), 52.98, 136.41, 136.50, 222.37. HRMS calcd for C₁₇H₂₉DO 251.2359, found 251.2362.

2,5-Bis(trimethylsilyl)-3,4-dihexyl-3-cyclopentenone (2b): Light yellow liquid, a mixture of cis and trans isomers in a ratio of 5:1. Combined isolated yield 70% (276 mg). ¹³C NMR (CDCl₃) for the main product: δ -0.59 (2SiMe₃), 14.02 (2CH₃), 22.58, 27.81, 27.96, 29.12, 31.66, 53.11, 133.30, 217.16. HRMS calcd for C₂₃H₄₆OSi₂ 394.3087, found 394.3092.

Bicyclic compound **2c**: Light yellow liquid, a mixture of cis and trans isomers in a ratio of 4:1. Combined isolated yield 71% (176 mg). ¹H NMR (CDCl₃) for the main product: δ 0.61-0.92 (m, 6H), 1.00-1.32 (m, 8H), 1.41-1.74 (m, 8H), 1.84-2.11 (m, 4H), 2.64 (t, J = 6.0 Hz, 2H). ¹³C NMR (CDCl₃) for the main product: δ 13.86, 22.75, 22.98, 24.11, 28.55, 28.74, 54.34, 135.21, 222.18. HRMS calcd for C₁₇H₂₈O 248.2140, found 248.2151.

2,3-Dibutylcyclopenten-1-one (2d): Colorless liquid. Isolated yield 79% (153mg). ¹H NMR (CDCl₃): δ 0.82 (t, J = 6.8 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H), 1.14-1.49 (m, 8H), 2.09 (t, J = 7.0 Hz, 2H), 2.26-2.42 (m, 6H). ¹³C NMR (CDCl₃): δ 13.74, 13.76, 22.66, 22.68, 22.75, 28.83, 29.55, 30.70, 30.78, 34.11, 140.33, 173.76, 209.87. These data are consistent with those reported.⁴

2,3-Dibutyl-4-deutero-cyclopenten-1-one (2dD): Colorless liquid. Isolated yield 74% (145mg). ¹H NMR (CDCl₃): δ 0.82 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H), 1.18-1.49 (m, 8H), 2.09 (t, J = 7.2 Hz, 2H), 2.26-2.40 (m, 5H). ¹³C NMR (CDCl₃): δ 13.78, 13.80, 22.69, 22.71, 22.79, 28.52 (t, J = 20.8 Hz), 29.57, 30.74, 30.81, 34.07, 140.40, 173.73, 209.95. HRMS calcd for C₁₃H₂₁OD 195.1733, found 195.1717.

A typical procedure for further reaction of the carbonylation reaction mixture with different reagents. Preparation of 2-methyl-2,3,4,5-tetrapropyl-3-cyclopentenone (3a) from the corresponding monolithio compound 1a.

To a THF-Et₂O (5ml, 1:1) solution of 1-iodo-1,2,3,4-tetrapropyl-1,3-butadiene (1.0 mmol) at -78°C was added *t*BuLi (2.0 mmol, 1.47 M in pentane). After this reaction mixture was stirred at -78 °C for 1h, CO gas was introduced from a CO cylinder and was bubbled for 10 min at -78 °C. The reaction mixture was then stirred under a slightly positive pressure of CO for 1h. After addition of MeI (1.0 mmol), the reaction mixture was warmed up to room temperature and stirred at room temperature for 1h. Hydrolysis of the reaction mixture with aqueous NH₄Cl and followed by normal workup afforded 2-methyl-2,3,4,5-tetrapropyl-3-cyclopentenone (**3a**) as a mixture of cis and trans isomers in a ratio of 3:2 in 90% combined isolated yield (238 mg). Light yellow liquid. ¹H NMR (CDCl₃) for the mixture: δ 0.79-1.01 (m, 15H), 1.24-1.71 (m, 12H), 1.76-2.39 (m, 4H), 2.67-2.89 (br, 1H). ¹³C NMR (CDCl₃) for the mixture: δ 14.08, 14.10, 14.43, 14.57, 14.77, 14.89, 18.29, 18.76, 19.19, 20.26, 20.75, 20.92, 23.01(CH₃), 23.68, 24.41 (CH₃), 27.65, 27.86, 28.42, 28.49, 30.72, 30.79, 38.59, 40.00, 51.05, 51.08, 52.94, 56.39, 56.44, 136.12, 136.43, 140.16, 224.95, 225.65. HRMS calcd for C₁₈H₃₂O 264.2453, found 264.2442.

2-Propargyl-2,3,4,5-tetrapropyl-3-cyclopentenone (3b): Light yellow liquid. Isolated yield 67% (193 mg). ¹H NMR (CDCl₃): δ 0.75-0.98 (m, 12H), 1.23-1.62 (m, 10H), 1.77-2.42 (m, 9H), 2.75-2.80 (br, 1H). ¹³C NMR (CDCl₃): δ 14.20, 14.40, 14.43, 14.97, 18.56, 20.40, 21.01, 23.33, 27.16, 27.93, 28.75, 30.80, 37.59, 52.67, 60.19, 69.96, 80.63, 136.36, 139.95, 222.86. HRMS calcd for C₂₀H₃₂O 288.2453, found 288.2456.

2-Benzyl-2,3,4,5-tetramethyl-3-cyclopentenone (3c): Yellow liquid. Isolated yield 78% (178mg). ¹H NMR (CDCl₃): δ 0.79 (d, *J* = 3.0 Hz, 3H), 1.01 (s, 3H), 1.39 (s, 3H), 1.49-1.72 (m, 4H), 2.62 (q, *J* = 13.2 Hz, 2H), 6.65-7.13 (m, 5H). ¹³C NMR (CDCl₃): δ 10.04, 11.52, 13.42, 22.00, 42.76, 49.86, 57.63, 126.10, 127.60, 129.42, 132.59, 133.37, 137.45, 223.85. HRMS calcd for C₁₆H₂₀O 228.1514, found 228.1510.

Bicyclic compound **3d**: Light yellow liquid. Isolated yield 75% (277mg). ¹H NMR (CDCl₃): δ -0.41 (s, 9H, SiMe₃), 0.00 (s, 9H, SiMe₃), 0.73-2.32 (m, 9H), 2.91 (q, *J* = 13.8 Hz, 2H), 6.92-7.16 (m, 5H). ¹³C NMR (CDCl₃): δ -3.06, -1.56, 22.93, 23.39, 25.74, 26.50, 34.15, 52.65, 62.14, 125.98, 128.03, 130.12, 132.21, 132.36, 139.63, 219.46. HRMS calcd for C₁₆H₂₀O 370.2148, found 370.2149.

Bicyclic compound **3e**: Light yellow liquid, a mixture of cis and trans isomers in a ratio of 10:1. Combined isolated yield 79% (227 mg). ¹H NMR (CDCl₃) for the main product: δ 0.70-0.89 (m, 6H), 1.08-1.75 (m, 16H), 1.79-2.22 (m, 6H), 2.31-2.47 (m, 1H), 4.76-4.94 (m, 2H), 5.33-5.57 (m, 1H). ¹³C NMR (CDCl₃) for the main product: δ 13.81, 13.84, 21.78, 22.63, 22.92, 22.98, 23.12, 24.21, 27.34, 28.46, 29.59, 34.76, 41.09, 54.77, 59.54, 117.19, 133.65, 135.85, 135.99, 224.06. HRMS calcd for C₂₀H₃₂O 288.2453, found 288.2431.

References

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