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The Synthesis of Cycloalkenes via Alkylidene-Mediated Olefin Metathesis and Carbonyl Olefination

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Supplementary Material: Experimental Section

General. ^{1}H spectra were recorded on a Bruker AM-500 spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million downfield from internal tetramethylsilane (δ scale), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, coupling constant (Hz), and assignment.

^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer at ambient temperature. ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale) with the solvent resonance employed as the internal standard ($CDCl_3$ at δ 77.0). All ^{13}C spectra were determined with complete proton decoupling.

Infrared spectra were obtained on a Perkin-Elmer 1600 Series FTIR. High resolution mass spectra were provided by the Southern California Mass Spectrometry Facility (University of California, Riverside). Analytical thin layer chromatography was accomplished using EM Reagents 0.25 mm silica gel 60 plates. Flash chromatography was performed on EM Reagents silica gel 60 (230-400 mesh).

Argon was purified by passage through a column of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. Benzene was distilled under argon from sodium benzophenone ketyl and stored under argon in a flask with a Teflon valve. **1** was prepared according to the method of Schrock.[1]

All reactions were conducted under an atmosphere of argon in oven-dried glassware with magnetic stirring.

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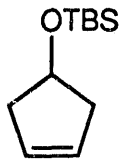
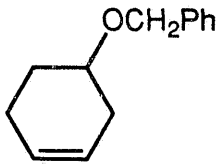
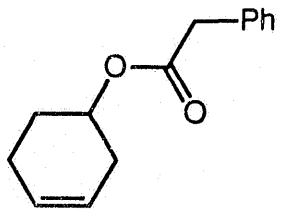


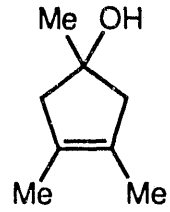
4-(*tert*-Butyldimethylsilyloxy)cyclopentene: IR (neat) 2957, 2928, 2856, 1471, 1462, 1361, 1256, 1082, 835, 808, 774 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 5.57 (br s, 2H, CHCH), 4.40 (apparent septet, 1H, J = 3.5, CHO), 2.43 (dd, 2H, J = 15.0, 6.8, CHHCHCHH), 2.23 (dd, 2H, J = 15.0, 3.6, CHHCHCHH), 0.96 (s, 9H, $C(CH_3)_3$), 0.04 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.71, 72.80, 43.02, 26.30, 18.62, -4.36.



4-(Benzyloxy)cyclohexene: IR (neat) 3026, 2921, 2842, 1496, 1453, 1437, 1360, 1097, 1028, 734, 696, 658 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.35-7.05 (m, 5H, aromatic H), 5.58 (m, 1H, CHCH), 5.51 (m, 1H, CHCH), 4.39 (d, 1H, J = 12.1, CHHPh), 4.36 (d, 1H, J = 12.1 CHHPh), 3.48 (m, 1H, CHO), 2.25-1.65 (m, 6H, $CH_2CH_2CHOCH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.67, 127.88, 127.73, 127.21, 124.65, 74.15, 70.24, 32.08, 28.21, 24.42. HRMS, *m/z* Calcd for $C_{13}H_{16}O_1$ (M^+): 188.1201 Found: 188.1204.



4-(Phenylacetyloxy)cyclohexene: ^1H NMR (500 MHz, C_6D_6) δ 7.25-7.05 (m, 5H, aromatic H), 5.47 (m, 1H, CHCH), 5.37 (m, 1H, CHCH), 5.02 (m, 1H, CHO), 3.37 (s, 2H, CH_2Ph), 2.20-1.55 (m, 6H, $CH_2CH_2CHOCH_2$). Identical to the product obtained from the acylation of 3-cyclohexen-1-ol with phenylacetyl chloride. HRMS, *m/z* Calcd for $C_{14}H_{17}O_2$ (MH^+): 217.1229 Found: 217.1234.



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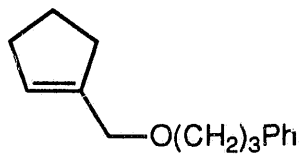
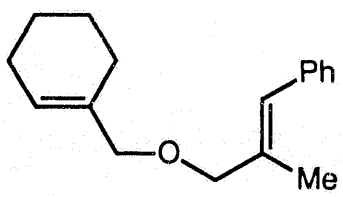
1,3,4-Trimethyl-3-cyclopenten-1-ol: IR (neat) 3332 (br), 2966, 2913, 1445, 1371, 1303, 1220, 1125, 1094, 934 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 2.29 (d, 2H, J = 15.6, CHHCCHH), 2.23 (d, 2H, J = 15.6, CHHCCHH), 1.47 (s, 6H, CCH_3CCH_3), 1.25 (s, 3H, $COCH_3$), 1.12 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.91, 77.11, 53.99, 28.25, 13.70. HRMS, *m/z* Calcd for $C_8H_{14}O_1$ (M^+): 126.1045 Found: 126.1040.

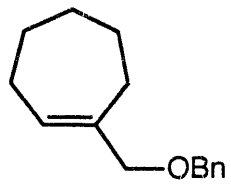


1-(3-(Phenyl)propyloxymethyl)cyclopentene: IR (neat) 3027, 2948, 28[illegible], 1496, 1454, 1359, 1100, 744, 698 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.20-7.05 (m, 5H, aromatic H), 5.61 (s, 1H, $CHCH_2$), 3.90 (s, 2H, CCH_2O), 3.27 (t, 2H, J = 6.1, OCH_2CH_2), 2.65-1.65 (m, 10H, $CHCH_2CH_2CH_2$, CH_2CH_2Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.18, 141.80, 128.58, 128.40, 127.42, 125.83, 69.80, 69.53, 33.07, 32.50, 31.51, 23.44. Calcd for $C_{15}H_{21}O_1$ (MH^+): 217.1592 Found: 217.1602.



1-(Cyclohexenyl)methyl 2-methyl-3-phenyl-2-propenyl ether: IR (neat) 3024, 2924, 2837, 1494, 1445, 1348, 1074, 744, 698 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.25-7.05 (m, 5H, aromatic H), 6.63 (s, 1H, CHPh), 5.72 (br s, 1H, $CHCH_2$), 3.88 (s, 2H, CH_2OCH_2), 3.83 (s, 2H, CH_2OCH_2), 2.05-1.45 (m, 8H, $CH_2CH_2CH_2CH_2$), 1.83 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.62, 135.42, 134.93, 128.87,

128.03, 126.63, 126.31, 125.06, 75.81, 74.72, 25.99, 25.02, 22.53, 22.39, 15.50. J- 3801-my



1-(Benzyloxymethyl)cycloheptene: IR (neat) 3029, 2920, 2848, 1453, 1351, 1069, 734, 696 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.35-7.10 (m, 5H, aromatic H), 5.83 (t, 1H, J = 6.4, $CHCH_2$), 4.36 (s, 2H, CH_2CCH_2O), 3.82 (s, 2H, CH_2Ph), 2.15-1.40 (m, 10H, $CH_2CH_2CH_2CH_2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.46, 138.13, 129.42, 127.75, 127.17, 126.87, 75.62, 70.87, 31.86, 29.65, 27.77, 26.53, 26.17. HRMS, *m/z* Calcd for $C_{15}H_{20}O_1$ (M^+): 216.1514 Found: 216.1504.

References and Notes

1) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875-3886.