Supporting Information

Ruthenium-Catalyzed Cyclic Carbonylation of Allenyl Alcohols. Selective Synthesis of γ- and δ-Lactones

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General Information. ^1H NMR and ^{13}C NMR were reported on a JEOL JMN-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ) multiplicity (s = singlet, d = doublet, t = triplet, and m = multiplet), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer; absorptions reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using a Shimadzu GCMS-QP2000. Elemental analyses were performed using a Perkin Elmer 240C. Analytical GC was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Nakarai tesque). Mps were determined using a Yamato Melting Point Apparatus Model MP-21 and uncorrected. TLC was carried out with Merck precoated silica gel plates (Kieselgel G60 F_{254}).

Materials. All Solvents and regents were dried and purified prior to use according to standard procedures. **1a** was prepared

by the treatment of 1-ethynyl-1-cyclohexanol with paraformaldehyde in the presence of diisopropylamine and copper bromide.[1] Allenyl alcohols **2a**, **3a**, **4a**, and **9a** were obtained by the reaction of corresponding aldehydes or ketones with tetrahydro-2-(2-propynyloxy)-2H-pyran in the presence of n-BuLi followed by the trearment of $LiAlH_4$.[2] 2-Methoxy-2,3-allenyl alcohols **5a**, **6a**, **7a**, and **8a** were prepared by the reaction of methoxyallene with corresponding aldehydes and ketones in the presence of n-BuLi.[1] 3,4-Allenyl alcohols **10a** and **11a** were obtained by the treatment of 3,4-pentadienoate with $LiAlH_4$ or MeMgBr.[2] The following materials are known and the specra data in accord with the literature data: **1a**,[1] **2a**,[2] **3a**,[2] **4a**,[2] **5a**,[1] **6a**,[3] **7a**,[1] **8a**,[4] **9a**,[5] **10a**,[1] and **11a**.[1]

Typical Procedure. A 100-ml stainless autoclave was charged with 1-propa-1,2-dienylcyclohexan-1-ol (**1a**) (1 mmol, 138 mg), 1,4-dioxane (15 ml), triethylamine (1.5 mmol), and $Ru_3(CO)_{12}$ (0.01 mmol, 6 mg). The system was flushed with 30 atm of CO three times. Finally it was pressurized to 10 atm and stirred at 100 °C. After 8 hours had elapsed, the autoclave allowed to cool in water. The CO was then released. The contents were transferred to a round bottomed flask with ether and the volatiles were removed in vacuo. The residue was subjected to column chromatography on silica gel (eluent; benzene) to give 3-methyl-1-oxaspiro[4.5]dec-3-en-2-one (**1b**) (165 mg, 99% yield) as a white solid.

2(5H)-Furanones **1b**,[6] **2b**,[7] **3b**,[8] **4b**,[9] **5b**,[10] **7b**,[11] **8b**,[11] and 2-pyranone **10b**[12] are known compounds and have the spectral data in accord with those of the literature. **6b**, **9b** and **11b** are new compounds.

4-methoxy-3,5,5-trimethyl-2(5H)-furanone (6b). pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 6H), 1.99 (s, 3H), 4.12 (s 3H); ^{13}C NMR ($CDCl_3$) δ 8.4, 24.4, 58.9, 80.8, 94.8, 173.9, 177.0; IR (neat) 2985 m, 1751 s, 1670 s, 1467 m, 1392 m, 1366 w, 1336 m, 1294 m, 1239 w, 1194 m, 1167 m, 1076 m, 980 m, 898 w, 763 w, 681 w, 636 w; MS, m/z (relative intensity, %) 156 (28), 141 (100), 113 (61), 99 (17), 83 (46), 59 (30); Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.80; H, 7.95.

3-isopropyl-1-oxaspiro[4,5]-3-en-2-one (9b). White solid; mp 97-98 °C; ^{1}H NMR ($CDCl_3$) δ 1.16 (d, J = 6.8 Hz, 6H), 1.25-1.75 (m, 10H), 2.61-2.67 (m, 1H), 6.96 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.0, 22.5, 24.7, 25.3, 35.0, 85.7, 139.1, 150.5, 172.7; IR (KBr) 3077 w, 2932 m, 2856 m, 1748 s, 1448 m, 1367 m, 1303 w, 1273 w, 1230 m, 1151 w, 1093 w, 1046 m, 1031 m, 977 m, 922 m, 886 w, 856 w, 787 w, 770 w; MS, m/z (relative intensity, %) 194 (47), 152 (84), 151 (50), 138 (24), 123 (59), 95 (82), 81 (73), 79 (53), 67 (78), 55 (92); Anal. Calcd for $C_{10}H_{14}O_2$: C, 74.19; H, 9.34. Found: C, 74.44; H, 9.28.

5,6-dihydro-3,6,6-trimethyl-2H-pyran-2-one (11b). pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 6H), 1.93 (s, 3H), 2.39 (d, J = 6.0, 2H), 6.46 (d, J = 5.8, 1H); ^{13}C NMR ($CDCl_3$) δ 16.9, 27.6, 35.8, 80.1, 127.6, 137.4, 165.4; IR (neat) 2979 m, 2929 m, 2059 w, 1987 m, 1716 s, 1452 w, 1387 w, 1372 m, 1302 w, 1270 m, 1174 m, 1131 m, 1106 m, 1064 w, 987 w, 946 w, 889 w, 865 w, 819 w, 747 w; Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.76; H, 8.41.

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