Experimental

General Methods. Catalytic reactions were performed in anhydrous 1,4-dioxane (Aldrich) under an atmosphere of nitrogen at room temperature. NMR were obtained on a Varian spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR in $CDCl_3$ unless otherwise noted. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Gas chromatography was performed on a HP 5890 gas chromatography equipped with a 25 m polydimethylsiloxane capillary column. Flash column chromatography was performed employing 200-400 mesh silica gel (EM). Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). An authentic sample of **2** was obtained from Aldrich. $PdCl_2(MeCN)_2$ was prepared from $PdCl_2$ (Strem).[1] Substrates **1**,[2] 8-methyl-7-nonene-2,4-dione (Table 1, entry 11),[3] and ethyl 3-oxo-6-heptenoate (Table 1, entry 12)[4] and new substrates were prepared from the appropriate 1,3-diketone or β-keto ester and allylic halide or tosylate employing a modified published procedure unless otherwise noted.[5] The known compound 3-methyl-7-octene-2,4-dione (Table 1, entry 5) was prepared by an alternative route.[6] The enol:dione ratio for each compound was determined by ^{1}H NMR spectroscopy in $CDCl_3$. Only the resonances corresponding to the predominant tautomer are given.

Substrates

8-Nonene-3,5-dione (Table 1, entry 3). Enol:dione = 4:1. 8-Nonene-3,5-dione was synthesized from 5-hexen-2-one and methyl propionate in 12% yield employing a modified literature procedure.[7] ^{1}H NMR: δ 5.96-5.85 (m, 1 H), 5.59 (s, 1 H), 5.18-5.07 (m, 2 H), 2.47 (m, 4 H), 2.41 (q, J = 7.6 Hz, 2 H), 1.23 (t, J = 7.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 195.6, 193.6, 137.2, 115.8, 98.8, 37.9, 31.8, 29.8, 10.0. IR (neat, cm^{-1}): 3078, 2977, 2938, 2918, 1726, 1613, 1444, 1416, 1377, 1352, 1323, 1202, 1142, 1064, 994, 914. Anal. calcd (found) for $C_9H_{14}O_2$: C, 70.10 (70.21); H, 9.15 (9.25).

2,2-Dimethyl-8-nonene-3,5-dione (Table 1, entry 4). Enol:dione = 13:1. ^{1}H NMR: δ 5.87-5.77 (m, 1 H), 5.60 (s, 1 H), 5.08-4.97 (m, 2 H), 2.43-2.35 (m, 4 H), 1.16 (s, 9

H). $^{13}C\{^1H\}$ NMR: δ 200.4, 195.1, 137.3, 115.7, 95.5, 51.8, 38.4, 29.9, 27.6. IR (neat, cm^{-1}): 3079, 2968, 2927, 2874, 1697, 1620, 1455, 1362, 1275, 1221, 1133, 1087. Anal. calcd (found) for $C_{11}H_{18}O_2$: C, 72.49 (72.35); H, 9.95 (9.91).

3-Benzyl-7-octene-2,4-dione (Table 1, entry 6). Enol:dione = 1:1.3. 3-Benzyl-7-octene-2,4-dione was synthesized from 7-octene-2,4-dione (**1**) and benzyl bromide in 35% yield employing a modified literature procedure.[8] ^1H NMR: δ 7.30-7.14 (m, 5 H), 5.69 (tdd, J = 6.4, 10.4, 17.2 Hz, 1 H), 4.96-4.92 (m, 2 H), 4.00 (t, J = 7.6 Hz, 1 H), 3.15 (dd, J = 4.0, 7.6 Hz, 2 H), 2.46-2.36 (m, 2 H), 2.27-2.22 (m, 2 H), 2.12 (s, 3 H). $^{13}C\{^1H\}$ NMR: δ 205.2, 203.8, 136.8, 129.1, 129.0, 127.8, 127.1, 115.9, 69.8, 42.4. 34.7, 32.7, 27.5. IR (neat, cm^{-1}): 3083, 3072, 3028, 2933, 1728, 1697, 1643, 1603, 1495, 1454, 1358, 1259, 1183, 1162, 1092, 995, 915. Anal. calcd (found) for $C_{15}H_{18}O_2$: C, 78.23 (78.07); H, 7.88 (8.02).

***cis*-7-Nonene-2,4-dione (Table 1, entry 7).** A suspension of 5% Pd(0) on $CaCO_3$, poisoned by Pb (115 mg) and 7-nonyne-2,4-dione (780 mg, 5.13 mmol) in acetone (20 mL) was stirred under hydrogen (1 atm) overnight at room temperature, concentrated, and chromatographed (hexanes–ethyl acetate = 125:1) to give *cis*-7-nonene-2,4-dione (540 mg, 69%) as a slightly yellow oil.

For 7-Nonyne-2,4-dione: Enol:dione = 5:1. ^1H NMR : δ 5.52 (s, 1 H), 2.48-2.42 (m, 4 H), 2.05 (s, 3 H), 1.76-1.73 (m, 3 H). $^{13}C\{^1H\}$ NMR: δ 193.1, 190.8, 100.2, 77.7, 76.8, 38.1, 25.0, 15.2, 3.8. IR (neat, cm^{-1}): 2969, 2919, 1857, 2357, 1729, 1713, 1620, 1417, 1360, 1236, 1132, 1005. Anal. calcd (found) for $C_9H_{12}O_2$: C, 71.03 (71.04); H, 7.95 (7.90).

For *cis*-7-Nonene-2,4-dione. Enol:dione = 5:1. ^1H NMR: δ 5.53-5.46 (m, 1 H), 5.50 (s, 1 H), 5.38-5.32 (m, 1 H), 2.38-2.30 (m, 4 H), 2.05 (s, 3 H), 1.63-1.60 (m, 3 H). $^{13}C\{^1H\}$ NMR: δ 193.9, 191.7, 128.8, 125.7, 100.2, 38.3, 25.3, 23.3, 13.1. IR (neat, cm^{-1}): 3015, 2958, 2920, 2860, 1709, 1613, 1443, 1359, 1234, 1138, 1096, 1030, 998, 963, 929. Anal. calcd (found) for $C_9H_{14}O_2$: C, 70.10 (70.12); H, 9.15 (9.14).

***trans*-7-Nonene-2,4-dione (Table 1, entry 8).** Enol:dione = 6:1. ^{1}H NMR: δ 5.48 (s, 1 H), 5.47-5.36 (m, 2 H), 2.34-2.22 (m, 4 H), 2.04 (s, 3 H), 1.64-1.62 (m, 3 H). ^{13}C{^{1}H} NMR: δ 194.0, 191.5, 129.6, 126.4, 100.2, 38.6, 28.8, 25.2, 18.2. IR (neat, cm^{-1}): 3013, 2965, 2919, 2863, 1713, 1620, 1454, 1360, 1236, 1142, 967. HRMS (EI) calcd (found) for $C_9H_{14}O_2$ (M^+): 154.0994 (154.0995).

7-Dodecene-2,4-dione (Table 1, entry 9). Enol:dione = 5:1. ^{1}H NMR (300 MHz): δ 5.47 (s, 1 H), 5.45-5.35 (m, 2 H), 2.34-2.21 (m, 4 H), 2.03 (s, 3 H), 1.98-1.92 (m, 2 H), 1.31-1.24 (m, 4 H), 0.86 (t, J = 7.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 193.8, 191.5, 132,0, 128.2, 100.1, 38.4, 32.3, 31.8, 28.7, 25.1, 22.3, 14.1. IR (neat, cm^{-1}): 3056, 2956, 2925, 2855, 1706, 1616, 1436, 1361, 1236, 1148, 967. HRMS (EI) calcd (found) for $C_{12}H_{20}O_2$ (M^+): 196.1463 (196.1460).

8-Phenyl-7-octene-2,4-dione (Table 1, entry 10). Enol:dione = 5:1. ^{1}H NMR: δ 7.31-7.23 (m, 4 H), 7.19-7.16 (m, 1 H), 6.39 (d, J = 16.0 Hz, 1 H), 6.17 (td, J = 6.8, 16.0 Hz, 1 H), 5.49 (s, 1 H), 2.52-2.47 (m, 2 H), 2.46-2.40 (m, 2 H), 2.03 (s, 3 H). ^{13}C{^{1}H} NMR: δ 193.7, 191.4, 137.7, 131.2, 128.9, 128.8, 127.5, 126.4, 100.3, 38.3, 29.1, 25.2. IR (neat, cm^{-1}): 3080, 3057, 3024, 2919, 2849, 1948, 1881, 1806, 1725, 1705, 1620, 1494, 1445, 1416, 1359, 1304, 1254, 1234, 1136, 1077, 965, 784, 744, 693. Anal. calcd (found) for $C_{14}H_{16}O_2$: C, 77.75 (77.81); H, 7.46 (7.42).

Benzyl 3-oxo-6-heptenoate (Table 1, entry 13). Enol:dione = 1:13. ^{1}H NMR : δ 7.37-7.35 (m, 5 H), 5.77 (tdd, J = 6.6, 10.2, 17.0 Hz, 1 H), 5.18 (s, 2 H), 5.05-4.96 (m, 2 H), 3.49 (s, 2 H), 2.62 (t, J = 7.2 Hz, 2 H), 2.36-2.30 (m, 2 H). ^{13}C{^{1}H} NMR: δ 201.9, 167.2, 136.7, 135.5, 128.8, 128.7, 128.6, 115.8, 67.3, 49.5, 42.3, 27.6. IR (neat, cm^{-1}): 3067, 3032, 2976, 2930, 1742, 1716, 1641, 1497, 1454, 1409, 1374, 1313, 1268, 1223, 1152, 1081, 997, 915. Anal. calcd (found) for $C_{14}H_{16}O_3$: C, 72.39 (72.16); H, 6.94 (6.78).

Cyclohexanones

2-Acetylcyclohexanone (2). Enol:dione ≥ 15:1. A solution of $PdCl_2(MeCN)_2$ (19 mg, 0.07 mmol) and 7-octene-2,4-dione (**1**) (100 mg, 0.70 mmol) in 1,4-dioxane (28 mL) was stirred at room temperature for 16 h, concentrated, and chromatographed (hexanes–diethyl ether = 75:1) to give **2** (81 mg, 81%) as a colorless oil. ^{1}H NMR: δ 2.32-2.28 (m, 4 H), 2.10 (s, 3 H), 1.68-1.64 (m, 4 H). $^{13}C\{^1H\}$ NMR: δ 199.3, 182.3, 107.3, 31.4, 25.2, 24.6, 23.1, 21.9. Spectral data were identical to that of an authentic sample.

The remaining cyclohexanones were synthesized using a procedure analogous to that employed in the synthesis of **2**.

2-Propionylcyclohexanone (Table 1, entry 3).[9] Enol:dione ≥ 15:1. ^{1}H NMR: δ 2.43 (q, J = 7.2 Hz, 2 H), 2.33-2.29 (m, 4 H), 1.69-1.66 (m, 4 H), 1.10 (t, J = 7.2 Hz, 3 H). $^{13}C\{^1H\}$ NMR: δ 203.2, 180.6, 106.9, 31.1, 30.7, 24.0, 23.1, 22.0, 8.5.

2-(2',2'-Dimethylpropionyl)cyclohexanone (Table 1, entry 4).[10] Enol:dione ≥ 15:1. ^{1}H NMR: δ 3.95-3.92 (m, 1 H), 2.55-2.48 (m, 1 H), 2.39-2.31 (m, 1 H), 2.12-2.03 (m, 1 H), 2.00-1.90 (m, 3 H), 1.87-1.81 (m, 1 H), 1.70-1.62 (m, 1 H), 1.11 (s, 9 H). $^{13}C\{^1H\}$ NMR: δ 212.7, 208.5, 57.8, 45.4, 42.2, 31.3, 27.4, 26.0, 23.6.

2-Acetyl-2-methylcyclohexanone (Table 1, entry 5).[11] ^{1}H NMR: δ 2.49-2.46 (m, 1 H), 2.45-2.43 (m, 1 H), 2.34-2.26 (m, 1 H), 2.10 (s, 3 H), 2.01-1.94 (m, 1 H), 1.75-1.62 (m, 3 H), 1.49-1.46 (m, 1 H), 1.24 (s, 3 H). $^{13}C\{^1H\}$ NMR: δ 210.9, 207.9, 64.2, 41.6, 37.1, 27.6, 26.0, 22.6, 21.1.

2-Acetyl-2-benzylcyclohexanone (Table 1, entry 6). ^{1}H NMR: δ 7.24-7.20 (m, 3 H), 7.08-7.05 (m, 2 H), 3.16, 3.08 (ABq, J = 6.0 Hz, 2 H), 2.54-2.48 (m, 1 H), 2.39-2.33 (m, 1 H), 2.28-2.20 (m, 1 H), 2.09 (s, 3 H), 1.99-1.95 (m, 1 H), 1.73-1.70 (m, 1 H), 1.64-1.58 (m, 2 H), 1.46-1.39 (m, 1 H). $^{13}C\{^1H\}$ NMR: δ 209.8, 206.1, 136.5, 130.6, 128.5, 127.1, 69.0, 42.4, 40.3, 34.3, 27.3, 27.2, 22.5. IR (neat, cm^{-1}): 3085, 3061, 3028, 2941, 2866, 1956, 1881, 1811, 1713, 1693, 1603, 1495, 1453, 1434, 1358, 1311. Anal. calcd (found) for $C_{15}H_{18}O_2$: C, 78.23 (78.13); H, 7.88 (7.80).

2-Acetyl-3-methylcyclohexanone (Table 1, entry 7 and 8).[12] Enol:dione ≥ 15:1. ^{1}H NMR: δ 2.77-2.73 (m, 1 H), 2.35-2.31 (m, 2 H), 2.18 (s, 3 H), 1.84-1.75 (m, 1 H), 1.72-1.60 (m, 3 H), 1.10 (d, J = 6.8 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 198.3, 184.4, 113.2, 31.7, 30.3, 28.2, 24.2, 22.0, 17.0.

2-Acetyl-3-butylcyclohexanone (Table 1, entry 9).[13] Enol:dione ≥ 15:1. ^{1}H NMR: δ 2.50-2.46 (m, 1 H), 2.34-2.31 (m, 2 H), 2.15 (s, 3 H), 1.83-1.62 (m, 3 H), 1.55-1.50 (m, 1 H), 1.42-1.20 (m, 6 H), 0.90 (t, J = 7.0 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 198.0, 184.4, 113.3, 35.1, 33.5, 31.5, 30.4, 25.6, 24.2, 23.1, 16.9, 14.4.

2-Acetyl-3-phenylcyclohexanone (Table 1, entry 10).[14] Enol:dione ≥ 15:1. ^{1}H NMR: δ 7.33-7.29 (m, 2 H), 7.23-7.16 (m, 3 H), 3.93 (dd, J = 3.2, 5.6 Hz, 1 H), 2.45-2.42 (m, 2 H), 2.07-1.94 (m, 1 H), 1.85 (s, 3 H), 1.84-1.80 (m, 1 H), 1.60-1.53 (m, 2 H). ^{13}C{^{1}H} NMR: δ 201.4, 183.1, 145.7, 128.8, 128.2, 126.6, 109.9, 40.5, 32.4, 31.2, 25.7, 16.9.

2-Acetyl-3,3-dimethylcyclohexanone (Table 1, entry 11).[15] Enol:dione ≤ 1:15. ^{1}H NMR: δ 3.44 (s, 1 H), 2.57 (ddd, J = 6.4, 10.0, 16.4 Hz, 1 H), 2.31-2.25 (m, 1 H), 2.17 (s, 3 H), 2.04 (ddd, J = 4.4, 10.4, 14.8 Hz, 1 H), 1.95-1.89 (m, 1 H), 1.85-1.77 (m, 1 H), 1.41-1.35 (m, 1 H), 1.04 (s, 3 H), 0.95 (s, 3 H). ^{13}C{^{1}H} NMR: δ 208.1, 205.3, 75.1, 39.6, 39.5, 35.3, 33.9, 28.3, 26.4, 22.2.

2-Ethoxycarbonylcyclohexanone (Table 1, entry 12).[16] Enol:dione = 3:1. ^{1}H NMR: δ 12.24 (s, 1 H), 4.20 (q, J = 7.2 Hz, 2 H), 2.27-2.20 (m, 4 H), 1.70-1.64 (m, 2 H), 1.62-1.58 (m, 2 H), 1.29 (t, J = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 173.1, 172.3, 98.1, 60.5, 29.4, 22.8, 22.7, 22.3, 14.6.

2-Benzoxycarbonylcyclohexanone (Table 1, entry 13).[17] Enol:dione = 4:1. ^{1}H NMR: δ 12.16 (s, 1 H), 7.38-7.31 (m, 5 H), 5.21 (s, 2 H), 2.30-2.27 (m, 4 H), 1.70-1.66 (m, 2 H), 1.64-1.58 (m, 2 H). ^{13}C{^{1}H} NMR: δ 172.9, 172.8, 136.5, 128.9, 128.4, 128.2, 98.0, 66.0, 29.5, 22.7, 22.6, 22.2.

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