Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Ruthenium Hydride-Catalyzed Regioselective Addition of Aldehydes to Enones Leading to 1,3-Diketones

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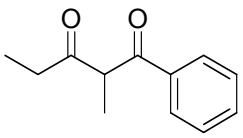
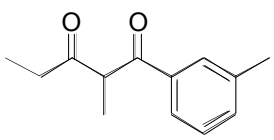
General: ^{1}H-NMR spectra were recorded with a JEOL JMN-500 (500 MHz) spectrometer in $CDCl_3$ and are referenced at 7.24 ppm for $CDCl_3$. ^{13}C-NMR spectra were recorded with a JEOL JMN-500 (125 MHz) spectrometer in $CDCl_3$ and are referenced at 77 ppm for $CDCl_3$. Chemical shifts are given in ppm. Conventional mass spectra were obtained on a Shimadzu GCMS-QP 5050A instrument and high resolution mass spectra were recorded with a JEOL JMS-700 spectrometer. Infrared spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions were reported in reciprocal centimeters. The products were purified by flash chromatography on silica gel (Nacalai Tesque Inc., Silica Gel 60, 230-400 mesh) and, if necessary, were further purified by preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) with GPC columns using $CHCl_3$ as an eluent. $RuHCl(CO)(PPh_3)_3$ was prepared from $RuCl_3 \cdot 3H_2O$ according to the reported procedure.[1] Other reagents were commercially available and used without further purification. The keto:enol ratio for each compound was determined by ^{1}H NMR spectroscopy in $CDCl_3$.

2-Methyl-1-phenylpentan-1,3-dione (3a).



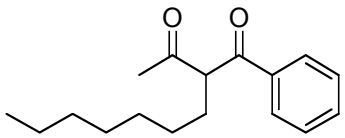
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.01 (t, 3H, *J* = 7.3 Hz), 1.44 (d, 3H, *J* = 6.9 Hz), 2.36-2.59 (m, 2H), 4.50 (q, 1H, *J* = 7.1 Hz), 7.48 (t, 2H, *J* = 7.8 Hz), 7.58 (t, 1H, *J* = 7.3 Hz), 7.96 (d, 2H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 7.75, 13.75, 34.16, 55.73, 128.66, 128.91, 133.65, 136.08, 197.59, 207.59; IR (neat) 3063, 1721, 1677, 1596, 1580 cm^{-1}; EIMS (relative intensity) *m/z* 190 (M^+), 161, 134, 105, 91, 77, 57; HRMS (EI) (*m/z*) calcd for $C_{12}H_{14}O_2$: 190.0994, found: 190.0993.

2-Methyl-1-(3-tolyl)pentan-1,3-dione (3b).



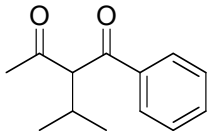
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.01 (t, 3H, *J* = 7.1 Hz), 1.42 (d, 3H, *J* = 7.3 Hz), 2.35-2.58 (m, 2H), 2.41 (s, 3H), 4.48 (q, 1H, *J* = 7.0 Hz), 7.34-7.40 (m, 2H), 7.73-7.77 (m, 2H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 7.76, 13.85, 21.46, 34.07, 55.91, 125.91, 128.72, 129.20, 134.41, 136.19, 138.83, 197.81, 207.70; IR (neat) 2980, 2938, 1720, 1675, 1603, 1585 cm^{-1}; EIMS (relative intensity) *m/z* 204 (M^+), 175, 148, 133, 119 (100), 91, 85, 83, 65, 57; HRMS (EI) (*m/z*) calcd for $C_{13}H_{16}O_2$: 204.1150, found: 204.1148.

2-Heptyl-1-phenylbutane-1,3-dione(3c).



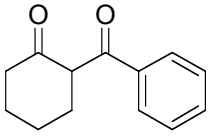
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.84 (t, 3H, *J* = 6.9 Hz), 1.21-1.27 (m, 10H), 1.90-2.02 (m, 2H), 2.12 (s, 3H), 4.40 (t, 1H, *J* = 7.1 Hz), 7.46 (t, 2H, *J* = 7.6 Hz), 7.57 (t, 1H, *J* = 7.3 Hz), 7.96 (d, 2H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.96, 22.51, 27.69, 27.71, 28.89, 29.04, 29.37, 31.62, 63.54, 128.60, 128.75, 133.57, 136.47, 196.44, 204.42; IR 1722, 1676, 1596, 1579 cm^{-1}; EIMS (relative intensity) *m/z* 260 (M^+), 218, 189, 162, 147, 133, 120, 105(100), 91, 77, 55; HRMS (EI) (*m/z*) calcd for $C_{17}H_{24}O_2$: 260.1776, found: 260.177.

2-Isopropyl-1-phenylbutane-1,3-dione (3d).



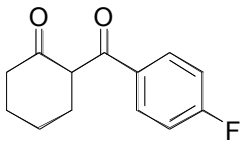
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.90 (d, 3H, *J* = 6.4 Hz), 0.97 (d, 3H, *J* = 6.4), 2.14 (s, 3H), 2.68-2.75 (m, 1H), 4.21 (d, 1H, *J* = 10.5 Hz), 7.47 (t, 2H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.8 Hz), 8.00 (d, 2H, *J* = 7.4 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 20.54, 21.15, 27.37, 29.73, 72.18, 128.87, 128.90, 133.74, 137.37, 196.37, 204.57; IR (neat) 3064, 1722, 1676, 1597, 1579 cm^{-1}; EIMS (relative intensity) *m/z* 204 (M^+), 186, 171, 147, 120, 105(100), 85, 77, 69, 51; HRMS (EI) (*m/z*) calcd for $C_{13}H_{16}O_2$: 204.1150, found: 204.115.

2-Benzoylcyclohexanone (3e). [2]



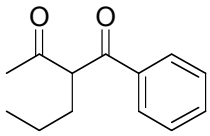
keto:enol = 40: 60 (keto-form was purified from keto-enol mixture by prepalative HPLC) keto-form: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.69-1.76 (m, 1H), 1.86-2.02 (m, 3H), 2.06-2.12 (m, 1H), 2.26-2.33 (m, 1H), 2.44-2.58 (m, 2H), 4.34-4.37 (m, 1H), 7.43 (t, 2H, *J* = 7.6 Hz), 7.54 (t, 1H, *J* = 7.6 Hz), 7.87 (d, 2H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 23.04, 27.27, 29.97, 42.23, 58.79, 128.47, 128.63, 133.23, 136.50, 197.50, 208.56; assignable peaks of enol-form: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.56-1.61 (m, 2H), 1.71-1.78 (m, 2H), 2.38 (t, 2H, *J* = 6.2 Hz), 2.46 (t, 2H, *J* = 6.7 Hz), 7.38-7.44 (two peaks overlap, 3H), 7.50-7.55 (two peaks overlap, 2H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 21.80, 23.37, 26.38, 32.62, 107.01, 127.50 128.03, 130.30, 137.38, 189.46, 191.29; IR (neat) 3060, 1712, 1682, 1598, 1583 cm^{-1}; EIMS (relative intensity) *m/z* 202 (M^+), 173, 156, 145, 125, 105(100), 91 77, 51; HRMS (EI) (*m/z*) calcd for $C_{13}H_{14}O_2$: 202.0994, found: 202.0992.

2-(4-Fluorobenzoyl)cyclohexanone (3f).



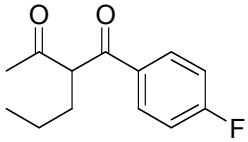
keto:enol = 54: 46 (obtained as an inseparable mixture) keto-form: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.71-1.79 (m, 1H), 1.89-2.05 (m, 3H), 2.06-2.12 (m, 1H), 2.27-2.33 (m, 1H), 2.44-2.57 (m, 2H), 4.31 (dd, 1H, *J* = 8.5, 5.8 Hz), 7.10 (dd, 2H, *J* = 17.9, 9.2 Hz), 7.92 (dd, 2H, *J* = 8.9, 5.3 Hz); assignable peaks of enol-form: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.58-1.63 (m, 2H), 1.71-1.79 (m, 2H), 2.39 (t, 2H, *J* = 6.2 Hz), 2.48 (t, 1H, *J* = 6.9 Hz),7.10 (dd, 2H, *J* = 17.9, 9.2 Hz), 7.56 (dd, 2H, *J* = 8.7, 5.5 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 21.89, 23.18, 23.52, 26.65, 27.33, 29.96, 32.71, 42.30, 58.85, 107.03, 115.30, 115.75, 130.11, 131.30, 133.10, 133.64, 163.94 (d, *J* = 251.4 Hz), 165.86 (d, *J* = 255.3 Hz), 189.70, 190.17; 195.90, 208.47; IR (KBr) 2947, 2871, 1705, 1597 cm^{-1}; EIMS (relative intensity) *m/z* 220 (M^+), 192, 163, 151, 123(100), 95, 75, 55; HRMS (EI) (*m/z*) calcd for $C_{13}H_{13}O_2F$: 220.0900, found: 220.0903.

1-Phenyl-2-propylbutane-1,3-dione (3g).



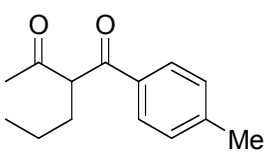
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.91 (t, 3H, *J* = 7.3 Hz), 1.28-1.33 (m, 2H), 1.90-2.00 (m, 2H), 2.11 (s, 3H), 4.42 (t, 1H, *J* = 7.1 Hz), 7.46 (t, 2H, *J* = 7.8 Hz), 7.57 (t, 1H, *J* = 7.3 Hz), 7.96 (d, 2H, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.87, 20.87, 27.72, 31.03, 63.20, 128.57, 128.76, 133.57, 136.44, 196.43, 204.34; IR (neat) 3063, 3027, 1722, 1676, 1596, 1579 cm^{-1}; EIMS (relative intensity) *m/z* 204 (M^+), 175, 162, 147, 133(100), 115, 105, 91, 77, 55; HRMS (EI) (*m/z*) calcd for $C_{13}H_{16}O_2$: 204.1150, found: 204.1150.

1-(4-Fluorophenyl)-2-propylbutane-1,3-dione (3h).



^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.93 (t, 3H, *J* = 8.4 Hz), 1.27-1.34 (m, 2H), 1.88-2.05 (m, 2H), 2.12 (s, 3H), 4.37 (t, 1H, *J* = 7.1 Hz), 7.12-7.16 (m, 2H), 8.00-8.03 (m, 2H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.96, 20.98, 27.62, 31.12, 63.49, 116.04, 131.52, 133.00, 166.10 ($J_{C\text{-}F}$ = 256.2 Hz), 194.85, 204.41; IR 3077, 1723, 1677, 1599 cm^{-1}; EIMS (relative intensity) *m/z* 222 (M^+), 193, 180, 151, 123 (100), 109, 95, 75, 55, 51; HRMS (EI) (*m/z*) calcd for $C_{13}H_{15}FO_2$: 222.1056, found: 222.1056.

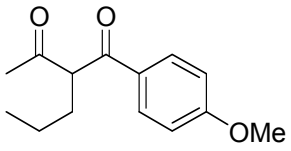
1-(4-Tolyl)-2-propylbutane-1,3-dione (3i).



^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.90 (t, 3H, *J* = 7.3 Hz), 1.26-1.32 (m, 2H), 1.87-2.01 (m, 2H), 2.10 (s, 3H), 2.39 (s, 3H), 4.39 (t, 1H, *J* = 7.1 Hz), 7.25 (d, 2H, *J* = 7.8 Hz), 7.86(d, 2H, *J* = 8.2 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.94, 20.91, 21.60, 27.69, 31.09, 63.20, 128.77, 129.47, 134.04, 144.64, 196.05, 204.62; IR (neat) 3032, 1723, 1672, 1606, 1573cm^{-1}; EIMS (relative intensity) *m/z* 218 (M^+), 203, 176(100), 161, 147,

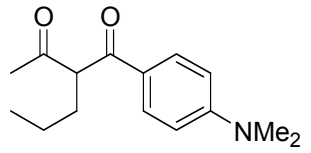
119, 91, 65, 55; HRMS (EI) (*m/z*) calcd for $C_{14}H_{18}O_2$: 218.1307, found: 218.1307.

1-(4-Methoxyphenyl)-2-propylbutane-1,3-dione (3j).



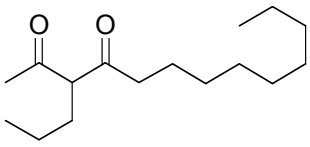
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.92 (t, 3H, *J* = 7.6 Hz), 1.26-1.34 (m, 2H), 1.87-2.04 (m, 2H), 2.11 (s, 3H), 3.86 (s, 3H), 4.37 (t, 1H, *J* = 7.1 Hz), 6.94 (d, 2H, *J* = 9.2 Hz), 7.97 (d, 2H, *J* = 8.7 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 14.02, 21.00, 27.67, 31.19, 55.57, 63.12, 114.07, 129.64, 131.14, 164.04, 194.88, 204.85; IR (neat) 1722, 1667, 1601, 1574 cm^{-1}; EIMS (relative intensity) *m/z* 234 (M^+), 192, 163, 135(100), 121, 92, 77, 64, 55; HRMS (EI) (*m/z*) calcd for $C_{14}H_{18}O_3$: 234.1256, found: 234.1256.

1-(4-Dimethylaminophenyl)-2-propylbutane-1,3-dione (3k).



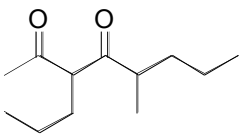
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.91 (t, 3H, *J* = 7.4 Hz), 1.26-1.34 (m, 2H), 1.86-2.03 (m, 2H), 2.10 (s, 3H), 3.06 (s, 3H), 4.33 (t, 1H, *J* = 7.2 Hz), 6.65 (d, 2H, *J* = 9.2 Hz), 7.90 (d, 2H, *J* = 9.2 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 14.08, 21.01, 27.73, 31.26, 40.03, 62.49, 110.79, 124.44, 131.06, 153.76, 194.05, 205.29; IR (KBr) 1704, 1653, 1652, 1618 cm^{-1}; EIMS (relative intensity) *m/z* 247 (M^+), 205, 176, 148 (100), 120, 105, 77, 55; HRMS (EI) (*m/z*) calcd for $C_{15}H_{21}NO_2$: 247.1572, found: 247.1572.

3-Propyltridecane-2,4-dione (3l).



keto: enol = 82: 18 (keto-form was purified by prepalative HPLC) keto-form: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.85 (t, 3H, *J* = 6.7 Hz), 0.89 (t, 3H, *J* = 7.3 Hz), 1.19-1.28 (m, 14H), 1.51-1.53 (m, 2H), 1.74-1.80 (m, 2H), 2.12 (s, 3H), 2.36-2.48 (m, 2H), 3.60 (t, 1H, *J* = 7.4); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.86, 20.86, 23.33, 28.58, 28.59, 28.61, 29.01, 29.20, 29.33, 29.41, 30.47, 42.32, 68.29, 69.32, 204.57, 206.63; assignable peak of enol-form: ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.86 (t, 3H, *J* = 6.9 Hz), 0.93 (t, 3H, *J* = 7.3 Hz), 1.19-1.33 (m, 14H), 1.35-1.43 (m, 2H), 2.11 (s, 3H), 2.36 (t, 1H, *J* = 7.6 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 14.04, 14.07, 22.65, 22.87, 24.16, 25.66, 29.17, 29.27, 29.36, 29.43, 29.48, 31.85, 35.20, 110.07, 190.88, 194.15; IR (neat) 1699, 1678, 1599 cm^{-1}; EIMS (relative intensity) *m/z* 254 (M^+), 225, 212, 183, 170, 155, 142, 127, 100 (100), 85, 71, 57; HRMS (EI) (*m/z*) calcd for $C_{16}H_{30}O_2$: 254.2246, found: 254.2247.

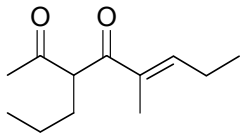
5-Methyl-3-propyloctane-2,4-dione (3m).



^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, 3H, *J* = 5.8 Hz), 0.91 (t, 3H, *J* = 7.1 Hz), 1.02-1.05 (m, 3H), 1.19-1.31 (m, 4H), 1.58-1.67 (m, 2H), 1.71-1.87 (m, 2H), 2.12 (d,

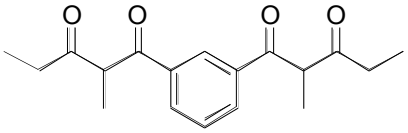
3H, *J* = 2.3 Hz), 2.62 (q, 1H, *J* = 6.7 Hz), 3.74 (td, 1H, *J* = 7.3, 5.0 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.94, 13.99, 14.04, 15.97, 16.02, 16.12, 16.17, 20.38, 21.06, 21.08, 23.44, 24.58, 27.99, 28.01, 28.06, 28.07, 29.05, 30.88, 31.01, 34.41, 34.77, 36.35 46.35, 67,22, 67.26, 67.29, 67.32, 109.59, 158.82, 158.93, 192.86, 196.63, 204.54, 204.65, 209.94, 210.04; IR (neat) 1698, 1727 cm^{-1}; EIMS (relative intensity) *m/z* 302 (M^+), 198, 156, 127, 114, 99, 85, 71, 55, 43 (100); HRMS (EI) (*m/z*) calcd for $C_{12}H_{22}O_2$: 198.1620 found: 198.1613

5-Methyl-3-propyl-5-nonene-2,4-dione (3n).



^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.89 (t, 3H, *J* = 7.3 Hz), 1.07 (t, 3H, *J* = 7.6 Hz), 1.19-1.26 (m, 2H), 1.74-1.89 (m, 5H), 2.06 (s, 3H), 2.23-2.29 (m, 2H), 4.15 (t, 1H, *J* = 7.1 Hz), 6.69 (t, 1H, *J* = 6.7 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 11.38, 12.89, 13.93, 20.89, 22.65, 27.38, 31.43, 61.75, 137.12, 146.72, 197.84, 205.06; IR (neat) 1660 cm^{-1}, 1722 cm^{-1}; EIMS (relative intensity) *m/z* 196 (M^+), 180, 154, 125, 107, 97 (100), 85, 83, 55; HRMS (EI) (*m/z*) calcd for $C_{12}H_{20}O_2$: 196.1463, found: 196.1460.

2-Methyl-1-[3-(2-methyl-3-oxopentanoyl)phenyl]pentane-1,3-dione (3o).



(keto-form was obtained as a major product) ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.03 (t, 6H, *J* = 7.3 Hz), 1.47 (d, 6H, *J* = 6.9 Hz), 2.44-2.63 (m, 4H), 4.54 (q, 2H, *J* = 7.0 HZ), 7.61 (t, 1H, *J* = 7.8 Hz), 8.17 (d, 2H, *J* = 7.8 Hz), 8.51 (s, 1H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 7.75, 13.65, 13.68, 34.22, 34.27, 55.99, 56.07, 128.54, 128.70, 129.68, 133.23, 136.63, 136.68, 196.52, 207.47; IR (neat) 1681, 1715 cm^{-1}; EIMS (relative intensity) *m/z* 302 (M^+), 246, 217, 190, 172, 160, 143, 131, 115, 104, 91, 76, 57; HRMS (EI) (*m/z*) calcd for $C_{18}H_{22}O_4$: 302.1518, found: 302.1516.

Deauterim Labeling Experiment

A mixture of ethyl vinyl ketone (**1a**) (74 mg, 0.88 mmol), benzaldehyde-*d* (**2a'**) (135 mg, 1.14 mmol), and $RuHCl(CO)(PPh_3)_3$ (85.3 mg, 0.09 mmol) in benzene (3 mL) was stirred at reflux for 5 h under an atmosphere of nitrogen. Purification by silica gel column chromatography gave deuterated 2-propanoylpropiophenone (**3a'**) (89.6 mg, 54%). Deuterium incorporation was determined by 1H NMR analysis. The absence of D2 compound was confirmed by EIMS analysis.

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