Supporting Information

Facile Oxidation of Aldehydes to Acids and Esters with Oxone

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General: All commercially available starting materials were purchased from Aldrich and used without further purification. Compound **22** was prepared as previously reported.¹ ¹H, ¹³C, 2D-COSY and DEPT spectra were recorded on 300 MHz NMR spectrometer (VARIAN INOVA) in CDCl₃. IR spectra were recorded on Nicolet IR/42 spectrometer using NaCl cells. Column chromatography was performed using Silicycle (40-60 μ m) silica gel. Analytical TLC was done using pre-coated silica gel 60 F₂₅₄ plates. GC analysis was performed using HP (6890 series) GC system (Column type-AltechSE-54, 30 m x 320 μ m x 0.25 μ m).

Experimental:

General Procedure for Oxidation of Aldehyde to Carboxylic Acid: The aldehyde (1 equiv) was dissolved in DMF (0.1 M). Oxone (1 equiv) was added in one portion and stirred at RT for 3 h. The reactions were monitored by TLC and GC analysis. 1N HCl was used to dissolve the salts and EtOAc was added to extract the products. The organic extract was washed with 1N HCl (3x) and brine, dried over Na₂SO₄, and the solvent was removed under reduced pressure to obtain the crude product. Products were purified by silica gel column chromatography.

General Procedure for Oxidation of Aldehydes to Esters: The aldehyde (1 equiv) was dissolved in the appropriate alcoholic solvent (0.1 M). Oxone (1 equiv) was added and stirred at RT for 18 h. The reaction was monitored by TLC and GC analysis. 1N HCl was used to dissolve the salts and EtOAc was added to extract the products. The organic extract was washed with 1N HCl (3x) and brine, dried over Na₂SO₄, and the solvent was removed under reduced pressure to obtain the crude product. Products were purified by silica gel column chromatography.

Spectral Data:

Spectral properties of *4-Nitrobenzoic acid (1a)*, *4-Cyanobenzoic acid (2a)*, *4-Chlorobenzoic acid (3a)*, *mono-Methyl terephthalate (4a)*, *Benzoic acid (5a)*, *4-Methylbenzoic acid (6a)*, *3-Bromobenzoic acid (7a)*, *2-Chlorobenzoic acid (8a)*, *2-Nitrobenzoic acid (9a)*, *3-Nitrobenzoic acid (10a)*, *3-Hydroxybenzoic acid (11a)*, *4-Hydroxybenzoic acid (12a)*, *4-Methoxybenzoic*

acid (13a), 4-Hydroxyphenol (16), 4-Methoxyphenol (17), Hexanoic acid (18a), Nonanoic acid (19a), Isobutyric acid (20a), 1,1,1-Trimethyl acetic acid (21a), Adipic acid (22a), Cyclohexane carboxylic acid (23a), Methyl benzoate (5b), Ethyl benzoate (5c), n-Propyl benzoate (5d), Methyl hexanoate (18b), Ethyl hexanoate (18c), Methyl-4-nitrobenzoate (1b), Methyl-4-cyanobenzoate (2b), Methyl 4-chlorobenzoate (3b), Methyl 4-methylbenzoate (6b), Methyl 4-hydroxybenzoate (12b), Methyl 4-methoxybenzoate (13b), Methyl nonanoate (19b), Methyl 2-methylpropanoate (20b), Methyl 2,2-dimethylpropanoate (21b), Dimethyl adipate (22b), Cyclohexanecarboxylic acid methyl ester (23b) match those reported by Aldrich and comparison to authentic samples.

i-Propyl benzoate (**5e**):² ^1H NMR (CDCl_3 , 300 MHz): δ 8.02 (m, 2H), 7.43 (m, 3H), 5.24 (sept, 1H, $J = 6.3$ Hz), 1.34 (d, 6H, $J = 6.3$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 175.2, 132.2, 130.4, 129.0, 127.8, 67.9, 21.5; IR (neat, NaCl, cm^{-1}) 2981, 2938, 1716, 1276, 1103, 711; LRMS (70 eV, EI) m/z 164 $[\text{M}]^+$, 122 $[\text{M}-\text{C}_3\text{H}_6]^+$, 105 $[\text{M}-\text{OC}_3\text{H}_7]^+$.

4-Hydroxyphenyl formate (**14**):³ ^1H NMR (CDCl_3 , 300 MHz): δ 8.27 (s, 1H), 6.98(d, 2H, $J = 9.0$ Hz), 6.78 (d, 2H, $J = 8.9$ Hz), 5.35 (bs, 1H); mp = 56-58 $^{\circ}\text{C}$, [lit. 57 $^{\circ}\text{C}$].

4-Methoxyphenyl formate (**15**):^{4,6} ^1H NMR (CDCl_3 , 300 MHz): δ 8.26 (s, 1H), 7.03(d, 2H, $J = 9.0$ Hz), 6.89 (d, 2H, $J = 8.9$ Hz), 3.78 (s, 3H); mp = 31-33 $^{\circ}\text{C}$, [lit. 32-34 $^{\circ}\text{C}$].

i-Propyl hexanoate (**18e**):⁷ ^1H NMR (CDCl_3 , 300 MHz): δ 5.04 (m, 1H), 2.30 (m, 2H), 1.12-1.54 (m, 12H), 0.86 (bs, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 186.6, 50.9, 34.7, 31.7, 29.8, 22.6, 21.8, 14.0, 13.9; IR (neat, NaCl, cm^{-1}) 2956, 2930, 1729, 1457, 1375, 1176, 1108; LRMS (70 eV, EI) m/z 158 $[\text{M}]^+$, 116 $[\text{M}-\text{C}_3\text{H}_6]^+$, 99 $[\text{M}-\text{OC}_3\text{H}_7]^+$.

1,2,3,6-Tetrahydrobenzoic acid (**23a**):^{8,9} ^1H NMR (CDCl_3 , 300 MHz): δ 5.63-5.7 (m, 2H), 2.54-2.64 (m, 1H), 2.24-2.27 (m, 2H), 1.98-2.15 (m, 3H), 1.62-1.76 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 182.6, 126.7, 124.9, 39.1, 27.1, 24.8, 24.3; IR (neat, NaCl, cm^{-1}) 3027, 2926, 1705, 1438, 1306, 1238; LRMS (70 eV, EI) m/z 126 $[\text{M}]^+$, 108 $[\text{M}-\text{H}_2\text{O}]^+$, 81 $[\text{M}-\text{CO}_2\text{H}]^+$.

6-ethyl-4-oxo-4H-chromene-3-carboxylic acid (25a): ^1H NMR (CDCl_3 , 300 MHz): δ 13.50 (bs, 1H), 8.98 (s, 1H), 8.11 (s, 1H), 7.68 (dd, 1H, $J = 2.2, 8.5$ Hz), 7.55 (d, 1H, $J = 8.8$ Hz), 2.72 (q, 2H, $J = 7.7$ Hz), 1.24 (t, 3H, $J = 7.7$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 179.4, 164.3, 163.6, 155.1, 144.0, 136.3, 124.2, 122.7, 118.6, 112.7, 28.4, 15.3; IR (neat, NaCl, cm^{-1}) 3073, 2961, 2924, 2869, 1734, 1616, 1478, 1436, 1310; LRMS (70 eV, EI) m/z 218 $[\text{M}]^+$; HRMS (CI) calcd for $\text{C}_{12}\text{H}_{10}\text{O}_4$: 218.0579 m/z $[\text{M}+\text{H}]^+$, observed 218.0580 m/z ; mp = 133-135 $^\circ\text{C}$.

6-ethyl-3-hydroxychromene-4-one (26): ^1H NMR (CDCl_3 , 300 MHz): δ 8.03 (d, 1H, $J=2.2$), 7.97 (s, 1H), 7.47 (dd, 1H, $J=2.2, 8.8$), 7.36 (d, 1H, $J=8.8$), 6.80 (bs, 1H), 2.72 (q, 2H, $J=3.4$), 1.24 (t, 3H, $J=3.6$); ^{13}C NMR (CDCl_3 , 75 MHz): δ 173.4, 154.7, 141.7, 140.8, 138.7, 133.9, 123.3, 121.7, 118.2, 28.2, 15.4; IR (neat, NaCl, cm^{-1}) 3276, 2959, 1610, 1408, 1204, 1170; LRMS (70 eV, EI) m/z 190 $[\text{M}]^+$; HRMS (CI) calcd for $\text{C}_{11}\text{H}_{10}\text{O}_3$: 190.0630 m/z $[\text{M}+\text{H}]^+$, observed 190.0627 m/z ; mp = 119-121 $^\circ\text{C}$.

5-(*p*-Bromophenyl)-2(3*H*)-furanone (**28**):¹⁰ ¹H NMR (CDCl₃, 300 MHz): δ 7.51 (d, 2H, *J* = 8.5 Hz), 7.49 (d, 2H, *J* = 8.2 Hz), 5.78 (t, 1H, *J* = 2.7 Hz), 3.49 (d, 2H, *J* = 2.7 Hz); ¹³C NMR (CDCl₃, 75 MHz): δ 175.4, 153.0, 131.9, 131.6, 127.2, 126.2, 123.7, 98.3, 34.7, 14.2; IR (neat, NaCl, cm⁻¹) 2916, 2848, 1780, 1673; LRMS (70 eV, EI) *m/z* 238 [M]⁺, 240 [M+2]⁺; HRMS (CI) calcd for C₁₀H₇O₂Br: 237.9630 *m/z* [M+H]⁺, observed 237.9631 *m/z*; mp = exp. 124-127 °C, lit. 126-130 °C.

4-(*p*-Bromophenyl)-4-oxobutanoic acid (**29**):¹¹ ¹H NMR (CDCl₃, 300 MHz): δ 7.83 (d, 2H, *J* = 8.5 Hz), 7.59 (d, 2H, *J* = 8.7 Hz), 3.26 (t, 2H, *J* = 6.4 Hz), 2.81 (t, 2H, *J* = 6.4 Hz); ¹³C NMR (CDCl₃, 75 MHz): δ 196.8, 178.5, 132.0, 131.9, 131.7, 130.3, 129.6, 33.1, 27.9; IR (neat, NaCl, cm⁻¹) 3425, 3091, 2958, 2925, 1694, 1678, 1585, 1339, 1229; LRMS (70 eV, EI) *m/z* 256 [M]⁺, 183 [M-C₃H₅O₂]⁺; mp = 144-146 °C, [lit 148-150 °C].

Methyl 4-(p-bromophenyl)-4-oxobutanoate (30):¹²⁻¹⁴ ^1H NMR (CDCl_3 , 300 MHz): δ 7.80 (d, 2H, $J = 2.2$ Hz), 7.77 (d, 2H, $J = 2.0$ Hz), 3.65 (s, 3H), 3.22 (t, 2H, $J = 6.6$ Hz), 2.49 (t, 2H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 197.0, 173.2, 135.1, 131.9, 129.5, 128.4, 51.8, 33.2, 27.8; IR (neat, NaCl, cm^{-1}) 3024, 2952, 2916, 2848, 1736, 1688, 1586, 1218, 1171, 1070, 757; LRMS (70 eV, EI) m/z 270 $[\text{M}]^+$, 183 $[\text{M}-\text{C}_4\text{H}_7\text{O}_2]^+$; HRMS (CI) calcd for $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Br}$: 269.9892 m/z $[\text{M}+\text{H}]^+$, observed 269.9896 m/z ; mp = 48-50°C.

References:

- (1) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. In *Vogel's Textbook of Practical Organic Chemistry*; Fifth ed.; Longman Scientific & Technical: Essex, 1991, p 593.
- (2) Jackson, L. B.; Waring, A. J. *J. Chem. Soc.-Perkin Trans. 2* **1990**, 907.
- (3) Tsunokawa, Y.; Iwasaki, S.; Okuda, S. *Chem. Pharm. Bull.* **1983**, *31*, 4578.
- (4) Jacobsenbauer, A.; Simchen, G. *Tetrahedron* **1988**, *44*, 5355.
- (5) Venturello, C.; Gambaro, M. *J. Org. Chem.* **1991**, *56*, 5924.
- (6) Baumstark, A. L.; Beeson, M.; Vasquez, P. C. *Tetrahedron Lett.* **1989**, *30*, 5567.
- (7) Aimo, G.; Degani, I.; Fochi, R. *Synthesis* **1979**, 223.

- (8) Thom, C.; Kocienski, P.; Jarowicki, K. *Synthesis* **1993**, 475.
- (9) Martin, S. F.; Dappen, M. S.; Dupre, B.; Murphy, C. J. *J. Org. Chem.* **1987**, 52, 3706.
- (10) Bartlett, P. A. *J. Am. Chem. Soc.* **1976**, 98, 3305.
- (11) Mallory, F. B.; Luzik, E. D.; Mallory, C. W.; Carroll, P. J. *J. Org. Chem.* **1992**, 57, 366.
- (12) Sierra, M. A.; Mancheno, M. J.; Saez, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, 120, 6812.
- (13) Sierra, M. A.; del Amo, J. C.; Mancheno, M. J.; Gomez-Gallego, M. *J. Am. Chem. Soc.* **2001**, 123, 851.
- (14) Gutman, A. L.; Zuobi, K.; Bravdo, T. *J. Org. Chem.* **1990**, 55, 3546.