Transition-metal- and Organic-Solvent-Free: A Highly Efficient Anaerobic Process for Selective Oxidation of Alcohols to Aldehydes and Ketones in water

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Supplementary data

Experimental Section

General

^{1}H NMR spectra were recorded on 60/300 MHz Spectrometer. Chemical shifts are expressed in δ units relative to tetramethylsilane (TMS) signal as internal reference in $CDCl_3$. FTIR spectra were recorded in $CHCl_3$ or on KBr pellets. Commercially available I_2, KI and K_2CO_3 were used directly. Column chromatography was performed on silica gel (60-120 mesh) using ethyl acetate and hexane as eluent.

General Typical Experimental Procedure:

Experimental procedure for the large-scale production of Anisaldehyde:

In a 1-liter two–necked round bottom flask (equipped with magnetic stirrer and reflux condenser), 4-methoxybenzyl alcohol (13.8 gm, 0.1 mol), potassium carbonate (20.7 gm,

0.15 mol) and 200 ml water were added and the mixture was stirred at 90 ^{o}C for 5 minutes. An aqueous solution of KI (4.15 gm, 25 mol%) and I_2 (6.5 gm, 0.025 mol) in 200 ml water were added successively to it, and another 19 gm (0.075 mol) of powdered I_2 was added portion wise within five minutes, and the whole mixture was heated at 90^{o}C with stirring for 20 minutes. The reaction mixture was allowed to cool to room temperature and a 50 ml solution of brine was added to settle down the organic product layer. The organic product layer of the reaction mixture was separated from the aqueous layer and the crude anisaldehyde was fractionally distilled at its boiling point (248^{o}C) under nitrogen atmosphere, 13.1 gm, 95% yield.

Method A: In a 50 ml two–necked round bottom flask (equipped with magnetic stirrer and reflux condenser in oil-bath), alcohol (1 mmol), potassium carbonate (0.207 gm, 1.5 mmol) and 2 ml water were added and the mixture was stirred at 90 ^{o}C for 5 minutes. An aqueous solution of KI (0.042 gm, 25 mol%) and I_2 (0.06 gm, 0.25 mmol) in 2 ml water were added successively to it, and another 0.20 gm (0.75 mmol) of powdered I_2 was added portion wise within five minutes, and the whole mixture was heated at 90 ^{o}C with stirring for stipulated time. The product was extracted with ethyl acetate (2 x 10 ml), washed the organic layer with brine (2 x 15 ml), dried over anhydrous Na_2SO_4 and concentrated, purified by column chromatography on SiO_2 (60-120 mesh) using ethyl acetate/hexane mixture as eluent, distillation of the solvent under reduced pressure gave pure carbonyl compounds.

Method B: In a 50 ml two–necked round bottom flask (equipped with magnetic stirrer and reflux condenser), Alcohol (1 mmol), potassium carbonate (0.276 gm, 2 mmol)

and 2 ml water were added and the mixture was stirred at 90 ^{o}C with stirring for 10 minutes. An aqueous solution of KI (0.042 gm, 25 mol%) and I_2 (0.06 gm, 0.25 mmol) in 2 ml water were added successively to it, and another 0.20 gm (0.75mmol) of powdered I_2 was added portion wise within ten minutes, and the whole mixture was heated at 90^{o}C for stipulated time. The product was extracted with ethyl acetate (2x10 ml), washed the organic layer with brine (2 x 15 ml), dried over anhydrous Na_2SO_4 and concentrated, purified by column chromatography on SiO_2 (60-120 mesh) using ethyl acetate/hexane mixture as eluent, distillation of the solvent under reduced pressure gave pure carbonyl compounds.

Characterization Data:

Benzaldehyde (1). According to the general experimental general procedure of method **A**, benzyl alcohol gave 100 mg (95 % isolated yield) of benzaldehyde as liquid, ^{1}H NMR ($CDCl_3$, 60 MHz) δ 10.2 (s, 1H), 7.5-8.0(m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 192.0, 136.2, 134.4, 129.7, 129.0; FTIR ($CHCl_3$) 1696cm^{-1}.

4-Methoxybenzaldehyde (2): According to the general experimental general procedure of method **A**, 4-methoxybenzyl alcohol gave 4-methoxybenzaldehyde, 130mg (isolated yield; 96 %) as a liquid; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 9.87 (s, 1H), 7.83 (d, 2H), 7.0(d, 2H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 190.5, 164.5, 132.0, 130.0, 114.3, 55.4; FTIR ($CHCl_3$) 1684 cm^{-1}.

3, 4-Dimethoxybenzaldehyde (3): According to the general experimental general procedure of method **A**, oxidation of 3, 4-dimethoxybenzyl alcohol gave 3, 4-dimethoxybenzaldehyde as a solid M.p 44 ^{o}C; 149 mg (isolated yield; 90 %) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.86 (s, 1H), 6.97-7.5 (m, 3H), 3.97 (s, 3H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 191.34, 154.88, 150.01, 130.52, 127.31, 110.77, 109.29, 77.88, 77.46, 77.03, 56.59, 56.41; FTIR ($CHCl_3$): 1682 cm^{-1}.

4-Nitrobenzaldehyde (4): According to the general procedure **A**, 4-nitrobenzyl alcohol gave 139 mg (92 %, isolated yield) of 4-nitrobenzaldehyde as a solid, M.p.107-108 ^{o}C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 10.3 (s, 1H), 8.3 (d, 2H), 8.0 (d, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 190.2, 151.1, 140.1, 130.4, 124.3; FTIR (KBr) 1680 cm^{-1}.

***p*-Chlorobenzaldehyde (5).** According to the general procedure, *p*-chliorhbenzyl alcohol gave 126 mg (90 %, isolated yield) of *p*-chlorobenzaldehyde as a solid, M.p.47-50 ^{o}C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 9.8 (s, 1H), 7.5-7.75 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 190.5, 140.7, 130.8, 129.4, 124.9; FTIR (KBr) 1687 cm^{-1}.

Cinnamaldehyde (6): According to the general experimental general procedure of method **A**, cinnamyl alcohol gave Cinnamaldehyde as a liquid; 105 mg (isolated yield; 80 %) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.7 (d, 1H), 7.4-7.5 (m, 5H), 6.5-6.7 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 193.4, 152.6, 133.8, 131.1, 129.0, 128.4, 128.3; FTIR ($CHCl_3$) 1681 cm^{-1}.

Furfural (7): According to the general experimental general procedure of method **A**, 2-furfural alcohol gave furfural as a liquid; 77 mg, (isolated yield 80 %). ^{1}H NMR (60 MHz, $CDCl_3$): δ 9.7(s, 1H), 7.7(s, 1H), 7.28 (s, 1H), 6.6 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 177.8, 152.9, 148.1, 121.1 112.6; FTIR: ($CHCl_3$) 1682 cm^{-1}.

Heptanal (8): According to the general experimental general procedure of method **B**, 1-heptanol gave heptanal as a liquid; 57 mg, (isolated yield 50 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.8(t, 1H), 2.4(m, 2H), 1.1-1.6 (m, 8H), 0.9 (t, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 202.7, 43.9, 31.6, 28.8, 22.5, 22.1, 13.9; FTIR: ($CHCl_3$) 1724 cm^{-1}. .

Decanal (9): According to the general experimental general procedure of method **B**, 1-decanol gave decanal as a liquid; 62 mg, (isolated yield 40 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.9(t, 1H), 2.2-2.5(m, 2H), 1.2-1.7 (m, 14H), 0.9 (t, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 202.2, 42.9, 31.5, 29.7, 29.4, 29.3, 29.2, 22.5, 22.0, 14.6; FTIR: ($CHCl_3$) 1721 cm^{-1}.

Cyclohexanone (10): According to the general experimental general procedure of method **B**, cyclihexanol gave cyclohexanone, 73.5 mg (isolated yield; 75 %) as a liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.3-2.4 (m, 4H), 1.7-1.9 (m, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 211.7, 41.9, 27.1, 25.0; FTIR ($CHCl_3$): 1715.4 cm^{-1}.

2, 6 Dimethylcyclohexanone (11): According to the general experimental general procedure of method **B**, 2, 6 dimethylcyclohexanol gave 2, 6 Dimethylcyclohexanone, 80 mg

(isolated yield; 64 %) as a liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.3-2.6 (m, 8H), 0.9 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 214.7, 42.9, 36.1, 23.2, 15.2; FTIR ($CHCl_3$): 1655 cm^{-1}.

Menthone (12): According to the general experimental general procedure of method **B**, menthol gave menthone as a liquid; 107 mg, (isolated yield 70 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.2-2.4 (m, 1H), 1.7-2.1(m, 6H), 1.4-1.6 (m, 2H), 0.7-1.0 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 212.0, 55.8, 50.6, 35.3, 27.8, 26.0, 22.2, 21.1, 18.7; FTIR: ($CHCl_3$) 1714 cm^{-1}.

6-Methoxy-1-tetralone (13): According to the general experimental general procedure of method **B**, 6-Methoxy-1, 2, 3, 4-tetrahydro-1-naphthol gave 6-methoxy-1-tetralone as a solid, M.p.78 ^{o}C; 132 mg (isolated yield; 75 %), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.01 (d, 1H), 6.8 (d, 1H), 6.7 (s, 1H), 3.85 (s, 3H), 2.9 (t, 2H), 2.58 (t, 2H), 2.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 197.64, 163.93, 147.37, 130.03, 126.72, 126.30, 113.44, 112.99, 77.89, 77.47, 77.04, 55.82, 39.30, 30.56, 23.78; FTIR (KBr) 1606 cm^{-1}.

4-isobutylacetophenone (14): According to the general experimental general procedure of method **B**, oxidation of 4-isobutyl-α-methylbenzyl alcohol gave 4-isobutyl acetophenone as a liquid; 149 mg, (isolated yield 76 %) ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81(d, 6H, $2CH_3$), 1.30-2.00(m, 1H), 2.40(d, 2H), 2.50(s, 3H), 6.90(d, 2H, aromatic-H), 7.55(d, 2H, aromatic-H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 197.85, 147.58, 135.08, 129.30, 128.31, 45.43, 26.50, 30.1, 22.35; FTIR: (neat) 1682 cm^{-1}.

Acetophenone (15): According to the general experimental general procedure of method **B**, oxidation of α-methylbenzyl alcohol gave acetophenone as a liquid; 96 mg (isolated yield; 80 %) ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.8-8.0 (m, 2H), 7.3-7.6 (m, 3H), 2.7 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 197.7,137.2, 133.1, 128.4, 128.1, 26.5; FTIR (film) 1695 cm^{-1}.