

A Novel Vanadium Catalyzed Oxidation of Alcohols to Aldehydes and Ketones under Atmospheric Oxygen

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Supporting Information

Experimental Section

General. Starting materials were purchased from Aldrich, Fluka and Lancaster and used without further treatment. V_2O_5 (99% purity with yellow to rust brown powder) was obtained from CDH (P) Ltd, Bombay. NMR spectra were recorded on DRX-300 (300 MHz for 1H and 75.5 MHz for ^{13}C) spectrophotometer using $CDCl_3$ as a solvent and Me_4Si as the internal standard. IR spectra were recorded on Nicolet impact 410 spectrophotometer. GC analysis was performed on HP-6890 series with a FID detector. Column chromatography was performed on silica gel (60-120 mesh) using ethyl acetate (or diethyl ether) and hexane as eluent.

Oxidation of Primary Alcohols. A mixture of primary alcohol (2 mmol), V_2O_5 (0.018 g, 5 mol%) and K_2CO_3 (1 mmol) was stirred in toluene (3 ml) at *ca.* 100 °C for the appropriate time under atmospheric oxygen. After removal of the catalyst and K_2CO_3 by filtration, the filtrate was analyzed by GC and then passed through a short pad of silica gel using ethyl acetate and hexane as eluent or distilled to afford the analytically pure aldehydes.

Oxidation of Secondary Alcohols. The oxidation of secondary alcohols to ketones was performed as above in the absence of K_2CO_3 .

All products were commercially available and identified by comparison of the isolated products with authentic samples.

Benzil. According to the general procedure benzoin gave 399 mg (95%) of the product as a yellow solid after column chromatography (ethyl acetate/hexane=1:19). M.p. 95 °C; 1H NMR ($CDCl_3$, 300 MHz) δ 7.8-8.0

(m, 4H), 7.6-7.7 (m, 2H), 7.3-7.5 (m, 4H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 195.1, 135.4, 133.6, 130.4, 129.6; IR (KBr) 1671 cm^{-1} .

Benzyl benzoate. According to the general procedure benzyl alcohol gave 206 mg (97%) of the product as a colorless liquid after column chromatography (ethyl acetate/hexane=1:19). ^1H NMR (CDCl_3 , 300 MHz) δ 8.0-8.2 (m, 2H), 7.3-7.6 (m, 8H), 5.4 (s, 2H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 166.3, 136.0, 132.9, 130.1, 129.6, 128.5, 128.3, 128.2, 128.1, 66.6; IR (neat) 1719 cm^{-1} .

Benzaldehyde. The oxidation was performed as described in the general procedure using 540 mg (5 mmol) of benzyl alcohol and the product was obtained 398 mg (75%) as a colorless liquid after distillation. ^1H NMR (CDCl_3 , 300 MHz) δ 10.2 (s, 1H), 7.5-7.9 (m, 5H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 192.2, 136.5, 134.4, 129.7, 128.9; IR (neat) 1695 cm^{-1} .

4-Methoxybenzaldehyde. According to the general procedure 4-methoxybenzyl alcohol provided 250 mg (92%) of the product as a colorless liquid after chromatography (ethyl acetate/hexane=1:19). ^1H NMR (CDCl_3 , 300 MHz) δ 9.9 (s, 1H), 7.8 (d, 2H, $J = 8.2\text{ Hz}$), 7.0 (d, 2H, $J = 8.2\text{ Hz}$), 3.9 (s, 3H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 190.6, 164.6, 131.9, 130.0, 114.3, 55.5; IR (neat) 1682 cm^{-1} .

4-Nitrobenzaldehyde. According to the general procedure 4-nitrobenzyl alcohol provided 238 mg (79%) of the product as a pale yellow solid after chromatography (ethyl acetate/hexane=1:19). M.p.: $105\text{ }^\circ\text{C}$; ^1H NMR (CDCl_3 , 300 MHz) δ 10.3 (s, 1H), 8.3 (d, 2H, $J = 8.3\text{ Hz}$), 8.0 (d, 2H, $J = 8.3\text{ Hz}$); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 190.2, 151.1, 140.1, 130.4, 124.3; IR (KBr) 1678 cm^{-1} .

3,4,5-Trimethoxybenzaldehyde. According to the general procedure 3,4,5-trimethoxybenzyl alcohol provided 368 mg (94%) of the product as a pale yellow solid after chromatography (ethyl acetate/hexane=1:9). M.p. $74\text{ }^\circ\text{C}$; ^1H NMR (CDCl_3 , 300 MHz) δ 9.9 (s, 1H), 7.1 (s, 2H), 3.9 (s, 9H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 190.9, 153.6, 143.7, 131.7, 106.8, 60.9, 56.3; IR (KBr) 1682 cm^{-1} .

Cinnamaldehyde. According to the general procedure cinnamyl alcohol provided 230 mg (87%) of the product as a yellow liquid after chromatography (diethyl ether/hexane=1:9). ^1H NMR (CDCl_3 , 300 MHz) δ 9.7 (d, 1H, $J = 7.7$ Hz), 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; IR (neat) 1681 cm^{-1} .

Geranial. According to the general procedure geraniol afforded 246 mg (81%) of the product as a colorless liquid after chromatography (diethyl ether/hexane=1:9). ^1H NMR (CDCl_3 , 300 MHz) δ 9.9 (d, 1H, $J = 8.1$ Hz), 5.8 (d, 1H, $J = 8.1$ Hz), 4.8-4.9 (m, 1H), 2.1-2.2 (m, 4H), 1.9 (s, 3H), 1.7 (s, 3H), 1.6 (s, 3H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 191.0, 163.5, 132.9, 127.2, 122.4, 40.5, 25.6, 25.5, 17.5, 17.4; IR (neat) 1678 cm^{-1} .

Heptanal. The oxidation was performed as described in the general procedure using 580 mg (5 mmol) of 1-heptanol and the product was obtained 228 mg (40%) as a colorless liquid after distillation. ^1H NMR (CDCl_3 , 300 MHz) δ 9.8 (t, 1H, $J = 7.3$ Hz), 2.4 (m, 2H), 1.1-1.6 (m, 8H), 0.9 (t, 3H, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 202.7, 43.9, 31.6, 28.8, 22.5, 22.1, 13.9; IR (neat) 1724 cm^{-1} .

Decanal. The oxidation was performed as described in the general procedure using 630 mg (4 mmol) of decanol and the product was obtained in 237 mg (38%) as a colorless liquid after distillation. ^1H NMR (CDCl_3 , 300 MHz) δ 9.9 (t, 1H, $J = 7.3$ Hz), 2.2-2.4 (m, 2H), 1.2-1.7 (m, 14H), 0.9 (t, 3H, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 202.5, 43.7, 31.7, 29.6, 29.5, 29.4, 29.3, 22.5, 22.1, 14.5; IR (neat) 1716 cm^{-1} .

Furfural. According to the general procedure furfural gave 163 mg (85%) of the product as a colorless liquid after chromatography (diethyl ether/hexane=1:9). ^1H NMR (CDCl_3 , 300 MHz) δ 9.7 (s, 1H), 7.7 (s, 1H), 7.3 (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; IR (neat) 1681 cm^{-1} .

2-Pyridinecarboxaldehyde. According to the general procedure pyridine-2-methanol gave 171 mg (80%) of the product as a pale yellow liquid after chromatography (ethyl acetate/hexane=1:9). ^1H NMR (CDCl_3 , 300 MHz) δ 10.3 (s, 1H), 8.7-8.8 (m, 1H), 7.8-8.0 (m, 2H), 7.5-7.6(m, 1H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 193.3, 152.7, 150.2, 137.0, 127.8, 121.6; IR (neat) 1716 cm^{-1} .

Acetophenone. The oxidation was performed as described in the general procedure using 1.2 g (10 mmol) of 1-phenylethanol and the product was obtained in 1.0 g (85%) as a colorless liquid after distillation. ^1H NMR (CDCl_3 , 300 MHz) δ 7.8-8.0 (m, 2H), 7.3-7.6 (m, 3H), 2.6 (s, 3H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 197.9, 137.2, 133.0, 128.5, 128.2, 26.5; IR (film) 1683 cm^{-1} .

Benzophenone. According to the general procedure diphenylmethanol gave 343 mg (94%) of the product as a colorless solid after chromatography (diethyl ether/hexane=1:9). M.p.: $48\text{ }^\circ\text{C}$; ^1H NMR (CDCl_3 , 300 MHz) δ 7.7-7.8 (m, 4H), 7.4-7.6 (m, 6H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 196.6, 137.5, 132.3, 129.9, 128.2; IR (KBr) 1661 cm^{-1} .

Cyclohexanone. The oxidation was performed as described in the general procedure using 990 mg (10 mmol) of cyclohexanol and the product was obtained in 735 mg (75%) as a colorless liquid after distillation. ^1H 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; IR (neat) 1717 cm^{-1} .

(+)-Menthone. According to the general procedure (+)-menthol gave 238 mg (77%) of the product as a colorless liquid after chromatography (diethyl ether/hexane=1:9). ^1H NMR (CDCl_3 , 300 MHz) 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, 55.7, 50.8, 35.3, 33.6, 27.8, 25.9, 22.2, 21.1, 18.7; IR (neat) 1714 cm^{-1} .

Cyclododecanone. According to the general procedure cyclododecanol gave 195 mg (81%) of the product as a colorless solid after chromatography (diethyl ether/hexane=1:9). M.p.: $58\text{ }^\circ\text{C}$; ^1H NMR (CDCl_3 , 300 MHz) δ 2.2-2.4 (m, 4H), 1.7-2.1 (s, 4H), 1.2-1.7 (m, 14H); IR (KBr) 1710 cm^{-1} .