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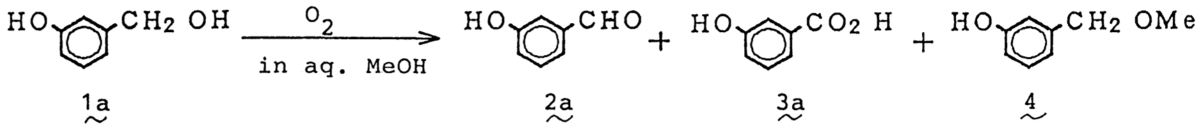
Selective Conversion of m-Hydroxybenzyl Alcohol to m-Hydroxybenzaldehyde

Ryu OI and Shinji TAKENAKA*
Omuta Research Institute, Mitsui Toatsu Chemicals, Inc.,
Omuta, Fukuoka 836

$Pt/C-CeCl_3-Bi_2(SO_4)_3$ catalyst system in aqueous methanol has been found to be effective for the selective oxygen oxidation of m-hydroxybenzyl alcohol to m-hydroxybenzaldehyde.

Recently, we have established an efficient electrochemical procedure for the synthesis of m-hydroxybenzyl alcohol (1a)1) from easily available m-hydroxybenzoic acid (3a), and we have now studied the application of 1a to the preparation of a useful synthetic intermediate, m-hydroxybenzaldehyde (2a). Hitherto, the oxidation of 1a with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)2) or chromium (VI) oxide-pyridine complex3) has been reported to give 2a in yields of 83% and 75% respectively, but the use of a stoichiometric amount of the expensive oxidizing agent is impractical. On the other hand, no catalytic oxidation of 1a to 2a has been appeared in the literature, whereas the oxygen oxidation of its isomer, o- or p-hydroxybenzyl alcohol (1b or 1c) was reported4) to produce corresponding benzaldehyde (2b or 2c) in good yield. Herewith, we describe the oxygen oxidation of 1a for the selective synthesis of 2a compared with that of 1b or 1c.



According to the reported procedure,5) 2b or 2c was selectively prepared from 1b or 1c (Table 1, entries 1 and 2), while the selectivity of 1a to 2a was low along with 3a by the further oxidation of desired 2a (entry 3) in the same reaction conditions. However, it is interesting to note that the selectivity to 2a was improved by the reaction in aqueous methanol (entry 4), and addition of $CeCl_3$ was further effective (entry 5).6)

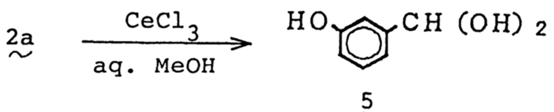
To a solution of 1a (40 mmol), $CeCl_3$-$7H_2O$ (0.1 g), $Bi_2(SO_4)_3$ (0.1 g), 3% Pt/C (0.5 g), and 93% NaOH (60 mmol) in 62.5% aqueous methanol (80 g) was purged oxygen under stirring at 50 °C for 2 h. After precipitates were filtered off, the mixture was poured into brine, acidified with cold 5% aqueous H_2SO_4, and extracted with diethyl ether. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was recrystallized from water to afford 2a (4.12 g, 98.5% purity, 83.0% yield).

Catalytic role of $CeCl_3$ in methanol is not clear, but this might protect the generated aldehyde (2a) from further oxidation by acetalization;7) formation of acetal (5) was observed by adding $CeCl_3$ from NMR analysis of 2a8) in CD_3OD/D_2O.

Table 1. Oxygen Oxidation of Hydroxybenzyl Alcohol(**1**)[a]

Entry	Substrate **1** 40 mmol	Solvent/g H_2O	 MeOH	Catalysts[b]	**1**(Recovery[c]/%)	Products[c](yield/%) **2**	 **3**	 **4**
1	**1b**	80	-	A	**1b**(trace)	**2b**(97)	**3b**(trace)	-
2	**1c**	80	-	A	**1c**(trace)	**2c**(98)	**3c**(trace)	-
3	**1a**	80	-	A	**1a**(2)	**2a**(42)	**3a**(55)	-
4	**1a**	30	50	A	**1a**(3)	**2a**(71)	**3a**(18)	(6)
5	**1a**	30	50	B	**1a**(2)	**2a**(88)	**3a**(1)	(5)

a) Oxygen was purged at 50 °C for 2 h. b) Catalysts A: 3% Pt/C (0.5 g) + $Bi_2(SO_4)_3$ (0.1 g), Catalysts B: 3% Pt/C (0.5 g) + $Bi_2(SO_4)_3$ (0.1 g) + $CeCl_3$-$7H_2O$ (0.1 g). c) Analyzed by HPLC based on **1**.



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3) J. R. Holum, J. Org. Chem., 26, 4814 (1961).
4) For example : a) P. S. Gradeff and S. T. Murayama, US Patent, US 4351962 (1982); Chem. Abstr., 97, 215746m (1982); b) T. Matsuo, T. Shirofuji, T. Murata, and H. Dandan, Jpn. Patent Kokai, 78-73532 (1978); Chem. Abstr., 89, 179705w (1978).
5) See Ref. 4a.
6) Small amount of methylbenzoate (**4**) was generated.
7) A. L. Gemal and J. L. Luche, J. Org. Chem., 44, 4187 (1979).
8) **2a**/**5** ratio was calculated from ^1H NMR; **2a**/**5**=8/2 (Analyzed in CD_3OD/D_2O(8/2)in the presence of 0.4% $CeCl_3$-$7H_2O$), **2a**/**5**=9/1 (Analyzed in CD_3OD/D_2O(8/2), No appreciable peak of **5** was detected in D_2O. ^1H NMR (CD_3OD/D_2O=8/2) δ =5.8 (1H, s, Ar-CH(O-$)_2$), 6.7-7.5 (4H, m, Ar-H), 9.8 (1H, s, CHO); ^{13}C NMR (CD_3OD/D_2O=8/2) with 0.4% $CeCl_3$-$7H_2O$) Mixture of **2a** and **5**; **2a**: δ =116.1 (d, C-2), 123.0 (d, C-6), 123.1 (d, C-4), 131.2 (d, C-5), 139.0 (s, C-3), 158.8 (s, C-1), 195.0 (d, C-7 (CHO)). **5**: δ =104.9 (d, C-7, (Ar-CH(O-$)_2$)), 114.5 (d, C-2), 116.6 (d, C-6), 119.1 (d, C-4), 130.3 (d, C-5), 140.7 (s, C-3), 157.9 (s, C-1).

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