Supporting Information
for DOI: 10.1055/s-0030-1259031
© Georg Thieme Verlag KG Stuttgart · New York 2010
Supporting Information

Regioselective Alkylation of Catechols Such as 3,4-Dihydroxybenzaldehyde via Mitsunobu Reactions
Xiaolong Wang,*a Tingting Ju,a Xiaodong Li,a Xiaoping Cao b
a School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, 730070, P. R. China
Fax +86(931)4956512; E-mail: wangxl@mail.lzjtu.cn
b Department of Chemistry, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, 730000, P. R. China

General Information

Reagents and solvents were all from commercial sources and used as received. 1H NMR and 13C NMR were determined in CDCl3 or acetone-d6 on a Mercury Plus 400 MHz spectrometer, tetramethylsilane (TMS) served as an internal standard.

General procedure for the regioselective alkylation under Mitsunobu conditions

DIAD (4.5 mmol) and Ph3P (4.5 mmol) were dissolved in dry THF (20 ml), and the solution was cooled in an ice bath. Alcohol (3 mmol) was added. After the mixture was stirred for 10 min, a solution of catechol (3 mmol) in dry THF (5 ml) was added immediately. After stirred for 30 min, the reaction mixture was warmed to room temperature and stirred. When the reaction was judged to be complete (TLC), the mixture was evaporated under vacuum and the residue was purified by column chromatography on silica gel eluting with a mixture of petroleum ether and ethyl acetate.

The 1H NMR and 13C NMR data of the products

4-Benzylolxy-3-hydroxybenzaldehyde (Entry 1, Table 1): 1H NMR (400 MHz, CDCl3): δ 5.20 (s, 2 H), 5.88 (br s, 1 H), 7.03 (d, J = 8.0 Hz, 1 H), 7.42 (m, 7 H), 9.83 (s, 1 H). 13C NMR (100 MHz, CDCl3): δ 71.3, 111.5, 114.4, 124.3, 127.9, 128.8, 128.9, 130.8, 135.2, 146.3, 191.0.

4-Allyloxy-3-hydroxybenzaldehyde (Entry 2, Table 1): 1H NMR (400 MHz, CDCl3): δ 4.70 (d, J = 5.6 Hz, 2 H), 5.41 (m, 2 H), 5.80 (s, 1 H), 6.06 (m, 1 H), 6.96 (d, J = 8.4 Hz, 1 H), 7.43 (m, 2 H), 9.84 (s, 1 H). 13C NMR (100 MHz, CDCl3): δ 69.9, 111.4, 114.3, 119.3, 124.3, 130.7, 131.8, 146.2, 150.7, 191.0.

3-Hydroxy-4-methoxybenzaldehyde (Entry 3, Table 1): 1H NMR (400 MHz, CDCl3): δ 3.96 (s, 3 H), 5.97 (s, 1 H), 6.95 (d, J = 8.0 Hz, 1 H), 7.41 (m, 2 H), 9.82 (s, 1 H). 13C NMR (100 MHz, CDCl3): δ 56.1, 110.2, 114.0, 124.6, 130.5, 146.1, 151.9, 191.1.

4-Butyloxy-3-hydroxybenzaldehyde (Entry 4, Table 1): 1H NMR (400 MHz, CDCl3): δ 1.00 (t, J = 7.6 Hz, 3 H),
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 13.7, 19.1, 31.0, 69.0, 110.9, 114.0, 124.5, 130.4, 146.2, 151.3, 191.0.

3-Hydroxy-4-phenethyloxybenzaldehyde (Entry 5, Table 1): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.13 (t, $J = 6.8$ Hz, 2 H), 4.30 (t, $J = 6.8$ Hz, 2 H), 6.09 (s, 1 H), 6.91 (d, $J = 8.4$ Hz, 1 H), 7.22–7.41 (m, 7 H), 9.77 (s, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 35.3, 69.5, 111.2, 114.2, 124.4, 126.7, 128.6, 128.7, 130.5, 137.1, 146.2, 151.0, 191.0.

3-Hydroxy-4-(p-methoxybenzyloxy)-benzaldehyde (Entry 6, Table 1): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.82 (s, 3 H), 5.08 (s, 2 H), 5.70 (br s, 1 H), 6.94 (m, 3 H), 7.33 (d, $J = 8.8$ Hz, 2 H), 7.59 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 51.9, 55.3, 71.0, 111.2, 114.2, 115.7, 122.7, 123.5, 126.8, 128.7, 128.8, 137.4, 145.4, 149.5, 166.7.

Methyl 4-butyloxy-3-hydroxybenzoate (Entry 10, Table 1): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.99 (t, $J = 7.2$ Hz, 3 H), 1.50 (m, 2 H), 1.82 (m, 2 H), 3.87 (s, 3 H), 4.10 (t, $J = 6.4$ Hz, 2 H), 5.71 (s, 1 H), 6.85 (d, $J = 9.2$ Hz, 1 H), 7.59 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 13.7, 19.1, 31.0, 51.9, 55.3, 71.0, 111.2, 114.2, 115.7, 122.7, 123.5, 126.8, 128.7, 128.8, 137.4, 145.4, 149.5, 166.7.

Methyl 3,5-dihydroxy-4-methoxybenzoate (Entry 13, Table 1): $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 3.81 (s, 3 H), 3.86 (s, 3 H), 7.09 (s, 2 H), 8.33 (s, 2 H). $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 52.7, 61.2, 110.3, 127.0, 140.9, 151.7, 167.5.
Copies of $^1$H NMR and $^{13}$C NMR Spectra for the Products

4-Benzyloxy-3-hydroxybenzaldehyde (Entry 1, Table 1)
4-Allyloxy-3-hydroxybenzaldehyde (Entry 2, Table 1)
3-Hydroxy-4-methoxybenzaldehyde (Entry 3, Table 1)
4-Butyloxy-3-hydroxybenzaldehyde (Entry 4, Table 1)
3-Hydroxy-4-phenethyloxybenzaldehyde (Entry 5, Table 1)
3-Hydroxy-4-(ρ-methoxybenzylxoy)-benzaldehyde (Entry 6, Table 1)
Methyl 4-benzyloxy-3-hydroxybenzoate (Entry 7, Table 1)
Methyl 4-allyloxy-3-hydroxybenzoate (Entry 8, Table 1)
Methyl 3-hydroxy-4-methoxybenzoate (Entry 9, Table 1)
Methyl 4-butyloxy-3-hydroxybenzoate (Entry 10, Table 1)
Methyl 3-hydroxy-4-phenethoxybenzoate (Entry 11, Table 1)
Methyl 3-hydroxy-4-(p-methoxybenzyl)oxy)-benzoate (Entry 12, Table 1)