Catalytic Deprotection of Protected Alcohols in Water Using Low-Loading and Alkylated Polystyrene-Supported Sulfonic Acid

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SUPPORTING INFORMATION

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General

Tetramethylsilane ($\delta = 0$) was used as an internal standard for ^1H NMR and CDCl_3 ($\delta = 77.0$) for ^{13}C NMR. The chemical shifts recorded on CD_3OD were reported relative to the

solvent; CHD₂OD (δ = 3.30) for ¹H NMR and CD₃OD (δ = 49.00) for ¹³C NMR. Distilled water was used as a solvent for aqueous reactions. The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literature.

Typical procedure for LL-ALPS-SO₃H-catalyzed deprotection of protected alcohols in water (Table 1 and 2). A mixture of dodecyl TBS ether (60.5 mg, 0.20 mmol) and the polymer-supported catalyst (LL-ALPS-SO₃H (0.172 mmol/g), 58.3 mg, 0.010 mmol) in degassed water (1.2 mL) was stirred for 12 h at 40 °C. The reaction mixture was quenched with saturated aq. NaHCO₃. The polymer was filtered and washed with water and ethyl acetate. The organic layer was dried over Na₂SO₄ and evaporated. The mixture was purified by preparative TLC on silica gel to give dodecanol (33.4 mg, 90%).

Dodecanol: ¹H NMR (CDCl₃) δ 0.88 (3H, t, J = 6.8 Hz), 1.26–1.40 (18H, m), 1.51 (1H, s), 1.52–1.59 (2H, m), 3.64 (2H, t, J = 6.7 Hz); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 25.8, 29.4, 29.5, 29.63, 29.64, 29.66, 29.68, 32.0, 32.8, 63.1.

4-Ethylphenol: ¹H NMR (CDCl₃) δ 1.20 (3H, t, J = 7.6 Hz), 2.57 (2H, q, J = 7.6 Hz), 4.69 (1H, br s), 6.75 (2H, d, J = 8.6 Hz), 7.06 (2H, d, J = 8.8 Hz); ¹³C NMR (CDCl₃) δ 15.8, 27.9, 115.1, 128.9, 136.6, 153.3.

4-Phenylbutan-2-ol: ¹H NMR (CDCl₃) δ 1.23 (3H, d, J = 6.3 Hz), 1.45 (1H, s), 1.74–1.80 (2H, m), 2.63–2.80 (2H, m), 3.80–3.85 (1H, m), 7.16–7.30 (5H, m); ¹³C NMR (CDCl₃) δ 23.6, 32.1, 40.8, 67.5, 125.8, 128.4, 142.0.

2-Methyl-4-phenylbutan-2-ol: ^1H NMR (CDCl_3) δ 1.29 (6H, s), 1.34 (1H, s), 1.77–1.82 (2H, m), 2.68–2.74 (2H, m), 7.15–7.31 (5H, m); ^{13}C NMR (CDCl_3) δ 29.4, 30.8, 45.8, 71.0, 125.8, 128.4, 128.5, 142.6.

2-Methylpentane-2,4-diol: ^1H NMR (CDCl_3) δ 1.20 (3H, d, $J = 6.1$ Hz), 1.27 (3H, s), 1.32 (3H, s), 1.49–1.53 (1H, m), 1.63–1.69 (1H, m), 2.95 (2H, br s), 4.18–4.25 (1H, m); ^{13}C NMR (CDCl_3) δ 24.4, 27.7, 32.2, 49.7, 65.8, 71.8.

Recycling experiment of LL-ALPS-SO₃H (eq 1). A mixture of dodecyl TBS ether (120.5 mg, 0.40 mmol) and LL-ALPS-SO₃H (0.172 mmol/g, 116.1 mg, 0.020 mmol) in degassed water (2.4 mL) was stirred for 12 h at 40 °C. The polymer was filtered through a glass filter, and then the polymer was washed with water and ethyl acetate. The organic layer was dried over Na₂SO₄, and evaporated. The mixture was purified by preparative TLC on silica gel to give dodecanol (66.4 mg, 89%). The recovered LL-ALPS-SO₃H was reused several times without loss of activity after being dried under vacuum.

Typical procedure for LL-ALPS-SO₃H-catalyzed selective deprotection of protected alcohols in water (Scheme 1). A mixture of Bn, TBS ether (58.9 mg, 0.20 mmol) and LL-ALPS-SO₃H (0.172 mmol/g, 58.1 mg, 0.010 mmol) in degassed water (1.2 mL) was stirred for 12 h at 40 °C. The reaction mixture was quenched with saturated aq. NaHCO₃. The polymer was filtered and washed with water and ethyl acetate. The organic layer was dried over Na₂SO₄ and evaporated. The mixture was purified by preparative TLC on silica gel to give 4-benzyloxybutan-1-ol (33.9 mg, 94%).

4-Benzyloxybutan-1-ol¹: ¹H NMR (CDCl₃) δ 1.64–1.75 (4H, m), 2.24 (1H, s), 3.52 (2H, t, *J* = 5.9 Hz), 3.64 (2H, t, *J* = 6.0 Hz), 4.52 (2H, s), 7.26–7.37 (5H, m); ¹³C NMR (CDCl₃) δ 26.7, 30.2, 62.7, 70.3, 73.1, 127.68, 127.73, 128.4, 138.1.

4-(*tert*-Butyldiphenylsilyloxy)butan-1-ol²: ¹H NMR (CDCl₃) δ 1.05 (9H, s), 1.62–1.71 (4H, m), 2.05 (1H, s), 3.64–3.72 (4H, m), 7.35–7.46 (6H, m), 7.59–7.61 (4H, m); ¹³C NMR (CDCl₃) δ 19.2, 26.8, 29.3, 29.8, 62.8, 64.0, 127.7, 129.6, 133.6, 135.6.

3-[4-(*tert*-Butyldimethylsilyloxy)phenyl]propan-1-ol: ¹H NMR (CDCl₃) δ 0.18 (6H, s), 0.98 (9H, s), 1.40 (1H, s), 1.82–1.89 (2H, m), 2.63 (2H, t, *J* = 7.7 Hz), 3.65 (2H, t, *J* = 6.5 Hz), 6.75 (2H, d, *J* = 8.6 Hz), 7.04 (2H, d, *J* = 8.3 Hz); ¹³C NMR (CDCl₃) δ -4.4, 18.2, 25.7, 31.2, 34.4, 62.3, 119.9, 129.2, 134.4, 153.7; IR (neat) 3348, 2930, 2858, 1510, 1255, 919, 841, 780 cm⁻¹; HRMS (EI) calcd for C₁₅H₂₆O₂Si (M⁺): 266.1702. Found: 266.1706.

Benzoic acid 5-hydroxy-1,3,4-tris(4-methoxybenzyloxy)pent-2-yl ester: ¹H NMR (CDCl₃) δ 1.95 (1H, br s), 3.62–3.81 (3H, m), 3.73 (3H, s), 3.76 (3H, s), 3.77 (3H, s), 3.86 (1H, dd, *J* = 5.4, 11.1 Hz), 3.93 (1H, dd, *J* = 3.4, 11.0 Hz), 4.04 (1H, dd, *J* = 4.9, 4.9 Hz), 4.40–4.53 (4H, m), 4.58 (1H, d, *J* = 11.0 Hz), 4.66 (1H, d, *J* = 11.2 Hz), 5.41–5.46 (1H, m), 6.76 (2H, d, *J* = 8.8 Hz), 6.80 (2H, d, *J* = 8.8 Hz), 6.81 (2H, d, *J* = 8.5 Hz), 7.17 (2H, d, *J* = 8.5 Hz), 7.20 (4H, d, *J* = 8.6 Hz), 7.40–7.45 (2H, m), 7.54–7.59 (1H, m), 7.98–7.81 (2H, m); ¹³C NMR (CDCl₃) δ 55.17, 55.22, 61.7, 67.9, 72.6, 72.9, 73.4, 73.8, 77.7, 78.5, 113.75, 113.77, 113.80, 128.4, 129.4, 129.7, 129.99, 130.01, 130.06, 130.10, 133.1, 159.20, 159.24, 159.4, 165.8; IR (neat) 3485, 2931, 1717, 1612, 1514, 1248, 1100, 1033, 820, 715 cm⁻¹; HRMS (FAB) calcd for C₃₆H₄₀O₉Na (M+Na⁺): 639.2570. Found: 639.2582.

LL-ALPS-SO₃H-catalyzed transprotection of dodecanol in water (eq 2). A mixture of dodecyl TBS ether (60.5 mg, 0.20 mmol), benzhydrol (73.8 mg, 0.40 mmol), and LL-

ALPS-SO₃H (0.172 mmol/g, 58.1 mg, 0.010 mmol) in degassed water (1.2 mL) was stirred for 24 h under reflux conditions. The polymer was filtered and washed with water and ethyl acetate after cooled to rt. The organic layer was dried over Na₂SO₄, and evaporated. The mixture was purified by preparative TLC on silica gel to give benzhydryl dodecyl ether³ (56.8 mg, 81%). ¹H NMR (CDCl₃) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.25–1.40 (18H, m), 1.60–1.67 (2H, m), 3.44 (2H, t, *J* = 6.6 Hz), 5.33 (1H, s), 7.21–7.36 (10H, m); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 26.3, 29.4, 29.5, 29.6, 31.9, 69.3, 83.6, 127.0, 127.3, 128.3, 142.7.

LL-ALPS-SO₃H-catalyzed esterification using dodecyl TBS ether in water (eq 3). A mixture of dodecyl TBS ether (60.5 mg, 0.20 mmol), hydrocinnamic acid (60.4 mg, 0.40 mmol), and LL-ALPS-SO₃H (0.172 mmol/g, 58.3 mg, 0.010 mmol) in degassed water (1.2 mL) was stirred for 48 h at 40 °C. The reaction mixture was quenched with saturated aq. NaHCO₃. The polymer was filtered and washed with water and ethyl acetate. The organic layer was dried over Na₂SO₄, and evaporated. The mixture was purified by preparative TLC on silica gel to give dodecyl hydrocinnamate⁴ (57.9 mg, 91%). ¹H NMR (CDCl₃) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26 (18H, s), 1.55–1.61 (2H, m), 2.62 (2H, t, *J* = 7.9 Hz), 2.95 (2H, t, *J* = 7.8 Hz), 4.05 (2H, t, *J* = 6.7 Hz), 7.16–7.31 (5H, m); ¹³C NMR (CDCl₃) δ 14.1, 22.7, 25.9, 28.6, 29.3, 29.4, 29.5, 29.6, 29.65, 29.67, 31.0, 31.9, 36.0, 64.7, 126.2, 128.3, 128.5, 140.6, 173.0.

LL-ALPS-SO₃H-catalyzed deprotection of the bisTBS ether in water (eq 4). A mixture of the bisTBS ether (73.3 mg, 0.20 mmol) and LL-ALPS-SO₃H (0.172 mmol/g, 57.9 mg, 0.010 mmol) in degassed water (1.2 mL) was stirred for 12 h at 40 °C. The reaction mixture was filtered, washed with water, and concentrated. *p*-Xylene glycol (27.4

mg, 99%) was obtained as an essentially pure form. Mp 118 °C; ¹H NMR (CD₃OD) δ 4.58 (4H, s), 4.86 (4H, s), 7.32 (4H, s); ¹³C NMR (CD₃OD) δ 65.0, 128.1, 141.7.

References

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SI-EXP. 914-2

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si-exp.1105-2

Date : Thu Jul 24 18:11:49 2003

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SI:Chemistry

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¹H-NMR

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