Supporting Information

Facile O-Deallylation of Allyl Ethers via S_N2' Reaction with *tert*-Butyllithium

William F. Bailey,*,† Michael D. England,‡ Michael J. Mealy,† Charnsak Thongsornkleeb,† and Lisa Teng†

Department of Chemistry, University of Connecticut, Storrs, CT 06269-3060, and the Department of Chemistry, Fairfield University, Fairfield, CT06430-5195

Experimental Section

General. Compound numbers, Tables, and references refer to those contained in the main body of the paper. All manipulations of alkyllithiums were performed in flame-dried glassware under a blanket of dry nitrogen using standard cannula and syringe techniques. The concentration of *t*-BuLi in pentane was determined by titration with a standard solution of 2-butanol in xylenes using 1,10-phenanthroline as indicator.[12] Diethyl ether and THF were freshly distilled from dark-purple solutions of sodium and benzophenone; olefin-free *n*-pentane, which was obtained by repeatedly washing commercial *n*-pentane with concentrated sulfuric

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acid until the acid layer remained clear, was washed with water and saturated sodium bicarbonate, dried over magnesium sulfate, and distilled immediately prior to use from a dark-purple solution of sodium / benzophenone containing tetraglyme.

Literature procedures, incorporating some minor modifications, were followed for the preparation of the following allyl ethers: 1-allyloxyhexane (Table 1, entry 1; bp 65 °C (16 mm) [lit.[13] bp 161–161.3 °C]), 2-allyloxyoctane (Table 1, entry 2; bp 75 °C (5.8 mm) [lit.[14] bp 77 °C (8 mm)]), allyl cholesteryl ether (Table 1, entry 3; mp 73–74 °C [lit.[15] mp 76–77 °C]), 1-allyloxyadamantane (Table 3, entry 4; bp 100–104 °C (1.5 mm) [lit.[16] bp 112 °C (2.6 mm)]), 1-allyloxy-4-(*t*-amyl)benzene (Table 1, entry 5; [bp (Kügelrohr) 150 °C (20 mm) [lit.[17] bp 142–143 °C (7 mm)]), 1-allyloxy-4-benzyloxybenzene (Table 1, entry 6; mp 58 °C [lit.[18] mp 57.5–58.0 °C]), and 3-*O*-allyl-1,2:5,6-di-*O*-isopropylidene-D-glucose[19] (Table 1, entry 7; bp (Kügelrohr) 105 °C (1.9 mm).

1-Allyloxy-4-(tetrahydropyran-2-yloxy)butane (Table 1, entry 8). A suspension of 2.04 g (85.0 mmol) of oil-free sodium hydride in 120 mL of dry THF was cooled to 0 °C under an atmosphere of nitrogen, 6.97 g (40.0 mmol) of 4-(tetrahydropyran-2-yloxy)butan-1-ol[20] was added, and the mixture was stirred at 0 °C for 15 min before addition of 4.20 mL (48.5 mmol) of allyl bromide. The reaction

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mixture was then stirred at room temperature for 20 h. Water was added to destroy any residual sodium hydride, the reaction mixture was filtered through a pad of Celite, and the filtrate was partitioned between water and diethyl ether. The organic layer was washed sequentially with 10 % aqueous sodium hydroxide, saturated, aqueous sodium bicarbonate, and brine, then dried (K_2CO_3) and concentrated under reduced pressure. Distillation of the residue gave 3.97 g (46 %) of the allyl ether as a colorless liquid: bp 75-85 °C (4.5 mm); ^{1}H NMR ($CDCl_3$): δ 1.50–1.61 (m, 4 H), 1.64–1.74 (m, 5 H), 1.78–1.86 (m, 1 H), 3.38–3.52 (m, 4 H), 3.73–3.78 (m, 1 H), 3.83–3.89 (m, 1 H), 3.96–3.98 (m, 2 H), 4.58 (t, J = 3.46 Hz, 1 H), 5.16 (dd, J = 10.46 Hz, J = 1.44 Hz, 1 H), 5.24–5.29 (m, 1 H), 5.87–5.96 (m, 1 H); ^{13}C NMR ($CDCl_3$): δ 19.49, 25.40, 26.38, 26.51, 30.64, 62.10, 67.16, 70.05, 71.68, 98.64, 116.54, 134.94; HRMS Calcd for $C_{12}H_{22}O_3$ 214.1569, found 214.1561.

1-Allyloxy-4-(*tert*-butyldimethylsilyloxy)butane (Table 1, entry 9). A suspension of 0.57 g (23.8 mmol) of oil-free sodium hydride in 80 mL of dry THF was cooled to 0 °C under an atmosphere of nitrogen, 2.38 g (11.7 mmol) of 4-(*tert*-butyldimethylsilyloxy)butan-1-ol[21] was added, and the mixture was stirred at 0 °C for 15 min before addition of 1.20 mL (13.9 mmol) of allyl bromide. The reaction mixture was then stirred at room temperature for 20 h and worked up as described above. Kügelrohr distillation of the residue afforded 2.33 g (82 %) of the allyl ether as a colorless liquid: bp 85 °C (7.8 mm); ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 6 H), 0.89 (s, 9 H), 1.55–1.66 (m, 4 H), 3.44 (t, J = 6.26 Hz, 2 H), 3.63 (t, J = 6.26 Hz, 2 H), 3.96 (ddd, J

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= 5.49 Hz, J = 1.41 Hz, J = 1.41 Hz, 2 H), 5.14–5.17 (m, 1 H), 5.23–5.29 (m, 1 H), 5.86–5.96 (m, 1 H); ^{13}C NMR ($CDCl_3$): δ –5.34, 18.30, 25.93, 26.20, 29.48, 62.95, 70.23, 71.73, 116.61, 135.03. Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.87; H, 11.55; Found C, 63.56; H, 11.98.

General Procedure for O-Deallylation of Allyl Ethers. A stirred solution of the allyl ether in dry *n*-pentane (typically 1 mL per mmol of ether) was cooled to –78 °C (dry ice – acetone bath), 1.1 molar equiv of *t*-BuLi in pentane was added via syringe, the cooling bath was then removed, and the solution was stirred for 1 h prior to the addition of 10 % aqueous hydrochloric acid (typically 1 mL per mmol of ether). The mixture was diluted with water and extracted with diethyl ether. The ethereal extract was washed with brine, dried ($MgSO_4$), and volatile components were removed at reduced pressure to afford essentially pure alcohol; yields are reported in Table 1.