

Photochemical Synthesis of Aldehydes in the Solid Phase

Ronald L Blankespoor,* Tim DeVries, Eric Hansen, Jeffrey M. Kallemeyn, Aaron M. Klooster, Jason A. Mulder, Robert P. Smart, and Douglas A. Vander Griend

Department of Chemistry and Biochemistry, Calvin College, Grand Rapids, Michigan

49546

blan@calvin.edu

Supporting Information Available: Experimental procedures and spectral data for 1-bromo-3-(4-nitrophenyl)propane, 1-iodo-3-(4-nitrophenyl)propane, and 3-(4-nitrophenyl)-1-propanol.

SUPPORTING MATERIALS

1-Bromo-3-(4-nitrophenyl)propane (14).

To a cold solution of conc. nitric acid (7 mL) and conc. sulfuric acid (8 mL) was slowly added 22.0 g (0.110 mol) of 1-bromo-3-phenyl propane. The reaction mixture was heated to 50 °C with vigorous stirring for 30 minutes. After cooling to room temperature the organic layer was washed with water (2x50 mL), diluted with 25 mL CH₂Cl₂, and washed with sat. Na₂CO₃. The organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure using a rotary evaporator to give a yellow liquid. Vacuum distillation gave 10.46 g (38.9%) **14**: bp 147-153 °C/0.6 torr; IR (film) 3108, 2943, 1599, 1529, 1437, 1242, 854, 803 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 8.13 (d, J = 8.85 Hz, 2H), 7.44 (d, J = 8.85 Hz, 2H), 3.43 (t, J = 6.41 Hz, 2H), 2.91 (t, J = 7.43 Hz, 2H), 2.17-2.26 (m, 2H); ¹³C NMR (250 MHz, CDCl₃) δ 148.54, 146.52, 129.42, 123.73, 33.81, 33.46, 32.63; MS (EI) m/e (rel intensity) 246 (12), 245 (100), 244 (12), 243 (100), 163 (50), 136 (100). Anal Calcd for C₉H₁₁BrNO₂: C, 44.29; H, 4.13; Br, 32.74; N, 5.74. Found: C, 44.37; H, 4.41; Br, 32.81; N, 5.88.

1-Iodo-3-(4-nitrophenyl)propane (15).

To a solution of NaI (7.863 g, 52.45 mmol) in 40 mL of acetone at reflux was added 1.98 g (8.10 mmol) of 1-bromo-3-(4-nitrophenyl)propane. A white precipitate formed almost immediately. After 17 hours, the reaction mixture was cooled, diluted with 30 mL of water and extracted with CHCl₃ (2x8 mL). The organic layers were combined, washed with water (2x8 mL), and dried over CaCl₂. Removal of solvent under reduced pressure in a rotary evaporator gave 2.32 g (98%) of **15** as a yellow liquid: IR (film) 3077, 2941,

2451, 1347, 1214, 857 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 8.15 (d, $J = 8.85$ Hz, 2H), 7.38 (d, $J = 8.85$ Hz, 2H), 3.18 (t, $J = 6.71$ Hz, 2H), 2.87 (t, $J = 7.18$ Hz, 2H), 2.10-1.24 (m, 2H); ^{13}C NMR (CDCl_3) δ 148.31, 146.62, 129.41, 123.80, 36.09, 34.12, 5.50.

3-(4-Nitrophenyl) 1-propanol (16).

To a solution of 4.00 g of silver nitrate in 200 mL of 1:1 water-dioxane was added 1.084 g (3.726 mmol) of 1-iodo-3-(4-nitrophenyl)propane resulting in the formation of a gray precipitate after a few minutes. The solution was heated to 45 °C for 2 hours. After cooling to room temperature, the precipitate was removed by vacuum filtration. The filtrate was diluted with 200 mL water and extracted with CH_2Cl_2 (3x100 mL). The extracts were combined, dried over CaCl_2 , and the solvent was removed under reduced pressure in a rotary evaporator. The residue was chromatographed on silica gel and eluted with 9:1 CH_2Cl_2 - hexane to yield 0.350 g (52.0%) of **16** as a yellow liquid: IR (film) 3443, 2939, 2875, 2450, 1503, 1344 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 8.06 (d, $J = 8.54$ Hz, 2H), 7.36 (d, $J = 8.55$ Hz, 2H), 3.68 (t, $J = 6.25$ Hz, 2H), 3.34 (br s, 1H), 2.84 (t, $J = 7.79$ Hz, 2H), 1.89-2.02 (m, 2H); ^{13}C NMR (250 MHz, CDCl_3) δ 149.92, 145.78, 129.03, 123.18, 61.07, 33.34, 31.70; MS (EI) m/e (rel intensity) 181 (8), 163 (100), 115 (33), 84 (83), 77 (33).