Supplementary Material (ESI) for Chemical Communications

Supporting Information

Regio- and stereospecific ring opening of 1,1-dialkyl-2-(aryloxymethyl)aziridinium salts by bromide

Matthias D'hooghe, Veronique Van Speybroeck, Michel Waroquier, Norbert De Kimpe*

Spectral data of compounds 9a, 12, 14a and 16.

2(*S*)-((3-Chlorophenoxy)methyl)-1-(1(*R*)-phenylethyl)aziridine **9a**. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46 (3H, d, J=6.6 Hz, CH_3); 1.60 (1H, d, J=6.6 Hz, H_a); 1.82-1.89 (1H, m, H_c); 1.95 (1H, d, J=3.3 Hz, H_b); 2.54 (1H, q, J=6.5 Hz, MeC*H*N); 3.79-3.90 (2H, m, CH_2O); 6.60-6.64, 6.73-6.74, 6.86-6.89, 7.09-7.14 and 7.24-7.40 (1H, 1H, 1H, 1H and 5H, 5×m, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.12 (CH_3); 32.41 (H_aCH_b); 36.74 (CH_c); 69.65 (Me*C*HN); 70.02 (CH_2O); 112.89, 114.95, 120.80, 126.76, 127.08, 128.27 and 130.05 (CH_{arom}); 134.65 (CCl); 144.18 (NCHC_{quat}); 159.32 (CO). IR (NaCl, cm-1): ν = 3062, 3028, 2974, 2926, 2869, 1594, 1484, 1232, 1030, 700. MS (70 eV) m/z (%): 287/9 (M^+, 2); 272/4 (5); 160 (35); 153 (23); 105 (100); 79 (10); 77 (12); 56 (10). Flash chromatography (SiO_2): Hexane/EtOAc 4/1, Rf = 0.18. α_D = -27.2° (c = 0.42, MeOH). 2(*R*)-((3-Chlorophenoxy)methyl)-1-(1(*R*)-phenylethyl)aziridine **12**. Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (1H, d, J=6.6 Hz, H_b); 1.46 (3H, d, J=6.6 Hz, CH_3); 1.70 (1H, d, J=3.6 Hz, H_a); 1.94-2.01 (1H, m, H_c); 2.52 (1H, q, J=6.6 Hz, MeC*H*N); 3.88 and 4.09 (2H, 2×d×d, J=4.4, 7.2, 10.3 Hz, (HCH)O); 6.82-6.86, 6.92-6.95, 6.98-7.00 and 7.17-7.40 (1H, 1H, 1H and 6H, 4×m, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.24 (CH_3); 31.16 (H_aCH_b); 38.25 (CH_c); 69.65 (Me*C*HN); 70.68 (CH_2O); 113.18, 115.21, 120.95, 126.77, 127.08, 128.36 and 130.15 (CH_{arom}); 134.79 (CCl); 144.27 (NCHC_{quat}); 159.57 (CO). IR (NaCl, cm-1): ν = 3061, 3028, 2971, 2926, 2869, 1595, 1479, 1231, 1031, 700. MS (70 eV) m/z (%): 287/9 (M^+, 2); 272/4 (3); 160 (31); 153 (20); 105 (100); 79 (7); 77 (10); 56 (8). Flash chromatography (SiO_2): Hexane/EtOAc 4/1, Rf = 0.48. α_D = +9.8° (c = 0.92, MeOH).

N-Benzyl-*N*-(2(*R*)-bromo-3-(3-chlorophenoxy)propyl)-(1(*R*)-*N*-phenylethyl)amine **14a**. Colorless viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, d, J=6.9 Hz, CH_3); 2.98 (2H, d, J=7.2 Hz, CHCH_2N); 3.59 (1H, d×d, J=6.5, 10.0 Hz, (*H*CH)O); 3.66 and 3.69 (2H, 2×d, J=13.5 Hz, Ar(HCH)N); 3.93-4.51 (3H, m, CHBr, CHN and (HC*H*)O); 6.59-6.64, 6.91-6.95 and 7.13-7.41 (2H, 1H and 11H, 3×m, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.92 (CH_3); 49.62 (CHBr); 54.02 (CHCH$_2$N); 56.00 (ArCH_2N); 58.13 (CHN); 70.13 (CH_2O); 113.23, 114.74, 121.03, 127.12, 127.26, 127.99, 128.13,

128.39, 128.88 and 129.98 (CH_{arom}); 134.66 (CCl); 139.43 and 142.45 (NCH_2C_{quat} and $NCHC_{quat}$); 158.88 (CO). IR (NaCl, cm-1): ν = 3062, 3028, 2970, 2932, 1596, 1481, 1453, 1428, 1232, 750, 699. MS (70 eV) m/z (%): no M^+; 378/80 (M^+-Br, 100). Flash chromatography (SiO_2): Hexane/EtOAc 9/1, Rf = 0.55. α_D = -7.3° (c = 2.06, CH_2Cl_2). *N*-Benzyl-*N*-(2(*S*)-bromo-3-(3-chlorophenoxy)propyl)-(1(*R*)-*N*-phenylethyl)amine **16**. Colorless viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43 (3H, d, J=6.9 Hz, CH_3); 2.88 and 3.16 (2H, 2×d×d, J=5.1, 9.4, 14.1 Hz, CH(*H*C*H*)N); 3.47 and 3.66 (2H, 2×d, J=13.6 Hz, Ar(HCH)N); 3.87-4.14 (4H, m, CHBr, CHN and CH_2O); 6.69-6.73, 6.78-6.80, 6.92-6.95 and 7.14-7.35 (1H, 1H, 1H and 11H, 4×m, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.25 (CH_3); 49.67 (CHBr); 54.48 (CH*C*H_2N); 55.99 (ArCH_2N); 59.91 (CHN); 69.84 (CH_2O); 113.17, 114.86, 121.14, 127.14, 127.17, 127.87, 128.16, 128.34, 128.80 and 130.10 (CH_{arom}); 134.71 (CCl); 139.50 and 141.95 (NCH_2C_{quat} and $NCHC_{quat}$); 158.91 (CO). IR (NaCl, cm-1): ν = 3063, 3028, 2972, 2933, 2838, 1595, 1480, 1453, 1247, 1231, 734, 700. MS (70 eV) m/z (%): no M^+; 378/80 (M^+-Br, 100). Flash chromatography (SiO_2): Hexane/EtOAc 29/1, Rf = 0.35. α_D = +25.1° (c = 1.47, CH_2Cl_2).