Supporting Information

Stereospecific Aziridination of Olefins via Electrophile-Induced Cyclization of γ,δ-Unsaturated Imines and Subsequent Hydrolytic Rearrangement

Matthias D'hooghe, Mark Boelens, Johan Piqueur and Norbert De Kimpe*

Department of Organic Chemistry, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium

3-(1-Isopropylaziridin-2-yl)-2,2-dimethylpropanal 8b. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.07-1.14 (12H, m, 4×CH_3); 1.24-1.46 (4H, m, NC*H*$_2$C*H*(*H*CH)); 1.87 (1H, d×d, J=12.8, 3.6 Hz, (HC*H*)CMe_2); 2.38 (1H, m, Me_2C*H*N); 9.51 (1H, s, HC=O). ^{13}C NMR (20 MHz, $CDCl_3$): δ 21.35, 21.90, 22.07 and 22.31 (4×Me); 33.69 (NCH_2); 34.63 (NCH); 41.43 (*C*H_2CMe_2); 45.79 (*C*Me_2); 61.22 (N*C*HMe$_2$); 204.79 (HC=O). IR (NaCl, cm^{-1}): $\nu_{C=O}$=1726. MS (70 eV) m/z (%): 169 (M^+, 1); 140 (7); 126 (22); 112 (5); 99 (6); 98 (78); 84 (8); 83 (5); 82 (7); 72 (10); 70 (7); 96 (5); 58 (18); 57 (8); 56 (100); 55 (12). Anal. Calcd for $C_{10}H_{19}NO$: C 70.96%; H 11.31%. Found: C 71.19%; H 11.43%.

3-(1-*tert*-Butylaziridin-2-yl)-2,2-dimethylpropanal 8c. Bp. 40-42°C/0.15 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 (9H, s, $(CH_3)_3$); 1.10 and 1.11 (6H, 2×s, $(CH_3)_2$C); 1.23 (1H, d, J=3.2 Hz, (H_{trans}CH)N); 1.49 (1H, d, J=6.1 Hz, (HCH_{cis})N); 1.52 (1H, m, CHN); 1.32 (1H, d×d, J=14.2, 7.7 Hz, (*H*CH)CMe_2); 1.88 (1H, d×d, J=14.2, 4.2 Hz, (HC*H*)CMe_2); 9.50 (1H, s, HC=O). ^{13}C NMR (20 MHz, $CDCl_3$): δ 21.36 and 22.15 ((*C*H_3)$_2$C); 26.66 ($(CH_3)_3$); 27.32 (NCH_2); 28.01 (NCH); 41.89 (*C*H_2CMe_2); 45.68 (*C*Me_2); 52.79 ($(CH_3)_3$*C*); 204.40 (HC=O). IR (NaCl, cm^{-1}): $\nu_{C=O}$=1725. MS (70 eV) m/z (%): 183 (M^+, 11); 168 (11); 140 (14); 127 (17); 126 (13); 112 (11); 108 (11); 98 (22); 96 (22); 84 (33); 83 (11); 82 (25); 81 (11); 71 (36); 70 (28); 69 (11); 67 (14); 58 (33); 57 (56); 56 (90); 55 (33). Anal. Calcd for $C_{11}H_{21}NO$: C 72.08%; H 11.55%. Found: C 71.92%; H 11.64%.

1-(1-*tert*-Butylaziridin-2-ylmethyl)-cyclohexanecarbaldehyde 10. Bp. 95°C/0.5 mmHg. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.94 (9H, s, $(CH_3)_3$); 1.22-1.97 (15H, m, $(CH_2)_5CCH_2CHCH_2$); 9.50 (1H, s, HC=O). ^{13}C NMR (68 MHz, $CDCl_3$): δ 22.41, 25.73, 27.73, 30.82 and 31.46 ($(CH_2)_5$); 26.63 ($(CH_3)_3$); 27.46 (NCH_2); 40.50 (CH_2C); 49.81 (C_{quat}); 52.90 ($(CH_3)_3C$); 206.57 (HC=O). IR (NaCl, cm^{-1}): $\nu_{C=O}$=1719. MS (70 eV) m/z (%): no M^+, 208 (M^+-Me, 20); 194 (10); 180 (18); 138 (19); 122 (16); 121 (12); 112 (16); 96 (21); 86 (20); 84 (16); 81 (35); 79 (15); 74 (51); 71 (15); 70 (16); 67 (21); 58 (57); 57 (63); 56 (100); 55 (21). Anal. Calcd for $C_{14}H_{25}NO$: C 75.28%; H 11.28%. Found: C 75.39%; H 11.13%.

3-(1-Isopropyl-3,3-dimethylaziridin-2-yl)-2,2-dimethylpropanal 12. Bp. 70°C/0.5 mmHg. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.05 and 1.07 (2×3H, 2×d, J=6.3 Hz, $(CH_3)_2CH$); 1.10 (9H, s, 3×CH_3); 1.22 (3H, s, CH_3); 1.25-1.30 (1H, m, CHN); 1.36 (1H, d×d, J=14.5, 9.9 Hz, *H*CH)CMe_2); 1.90 (1H, d×d, J=14.5, 2.6 Hz, (HC*H*)CMe_2); 2.16 (1H, septet, J=6.3 Hz, NC*H*Me_2); 9.49 (1H, s, HC=O). ^{13}C NMR (68 MHz, $CDCl_3$): δ 17.65, 20.74, 21.69, 22.23, 22.46 and 22.91 (6×CH_3); 36.82 (CH_2); 40.40 (C_{quat}); 44.89 (CHN); 44.96 (C_{quat}); 52.49 (NCH); 205.12 (HC=O). IR (NaCl, cm^{-1}): $\nu_{C=O}$=1721. MS (70 eV) m/z (%): 197 (M^+, 9); 182 (4); 168 (13); 154 (27); 127 (14); 126 (100); 112 (10); 98 (9); 97 (21); 84 (65); 72 (9); 71 (21); 70 (72); 69 (22); 68 (12); 58 (40); 57 (15); 55 (20). Anal. Calcd for $C_{12}H_{23}NO$: C 73.04%; H 11.75%. Found: C 73.14%; H 11.88%.

3-(1-Isopropyl-2-methylaziridin-2-yl)-2,2-dimethylpropanal 14. Bp. 65°C/0.03 mmHg. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.04 and 1.65 (2×1H, 2×s, (HCH)N); 1.06 (3H, s, CH_3); 1.07 and 1.09 (2×3H, 2×d, J=6.3 Hz, $(CH_3)_2CH$); 1.12 and 1.15 (2×3H, 2×s, 2×CH_3); 1.51 and 1.96 (2×1H, 2×d, J=14.8 Hz, CH_2); 2.10 (1H, septet, J=6.3 Hz, NCH); 9.53 (1H, s, HC=O). ^{13}C NMR (68 MHz, $CDCl_3$): δ 15.88, 21.42, 22.69, 23.11 and 23.49 (5×CH_3); 37.82 (C_{quat}); 39.86 (NCH_2); 46.02 (C_{quat}); 49.27 (CH_2); 52.74 (NCH); 205.60 (HC=O). IR (NaCl, cm^{-1}): $\nu_{C=O}$=1724. MS (70 eV) m/z (%): no M^+; 168 (M^+-Me, 4); 155 (17); 154 (28); 140 (17); 126 (19); 113 (16); 112 (90); 100 (13); 99 (14); 98 (16); 97 (10); 96 (18); 84 (27); 81 (15); 72 (19); 71 (20); 70 (100); 58 (33); 57 (13); 56 (68); 55 (34). Anal. Calcd for $C_{11}H_{21}NO$: C 72.08%; H 11.55%. Found: C 72.19%; H 11.67%.

7-*tert*-Butyl-2-methyl-7-azabicyclo[4.1.0]heptane-2-carbaldehyde 20. Bp. 80°C/0.03 mmHg. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.92 (9H, s, $(CH_3)_3$); 1.11 (3H, s, CH_3); 0.81-1.89 (7H, m, $(CH_2)_3CH$); 1.59 (1H, d, J=6.3 Hz, NC*H*CMe); 9.63 (1H, s, HC=O). ^{13}C NMR (68 MHz, $CDCl_3$): δ 16.50, 24.26 and 28.03 ($(CH_2)_3$); 20.90 (Me); 26.61 ($(CH_3)_3$); 29.15 and 35.85 (2×NCH); 43.68 (*C*Me_2); 52.63 (*C*Me_3); 205.37 (HC=O). IR (NaCl, cm^{-1}): $\nu_{C=O}$=1716. MS (70 eV) m/z (%): no M^+; 180 (M^+-Me, 4); 167 (11); 166 (13); 152 (35); 139 (32); 111 (12); 110 (100); 96 (16); 95 (50); 94 (11); 93 (13); 83 (31); 82 (14); 81 (13); 79 (10); 68 (12); 67 (16); 58 (99); 57 (36); 56 (17); 55 (25); 53 (10). Anal. Calcd for $C_{12}H_{21}NO$: C 73.80%; H 10.84%. Found: C 73.96%; H 10.69%.