SUPPORTING INFORMATION

Facile Preparation of α-Amino ketones from Oxidative Ring-Opening of Aziridines by Pyridine *N*-Oxide

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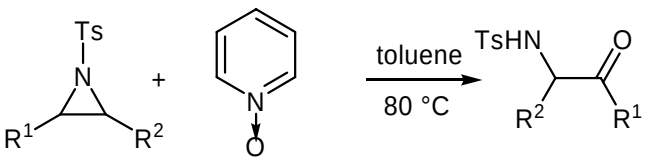
General Experimental Conditions. All reactions were performed in dry tube under an argon atmosphere if not noted. Toluene was redistilled with Na. Aziridines were prepared according to literature.[1] All of the other commercially available reagents were used as received without further purification. Melting points were not corrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 300 MHz and 90 MHz spectrometers, the chemical shifts were referenced to tetramethylsilane in $CDCl_3$. IR spectra were measured in cm^{-1}.

General procedure for the oxidative ring opening reaction of aziridines with pyridine *N*-oxide: To an oven-dried tube charged with aziridine **1** (0.5mmol), pyridine *N*-oxide (57 mg, 0.6 mmol) and toluene (2 mL) under Ar, the resulting mixture was warmed to 80°C and stirred at this temperature until the starting material **1** disappeared (monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by chromatography (silica gel: petroleum ether/AcOEt = 3:1) to afford α-amino carbonyl compounds **3.**



1 **2a** **3**

4-methyl-*N*-(2-oxo-cyclopentyl)-benzenesulfonamide (3a):[2] 77% yield; white solid; m.p. 122-123°C; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (ppm): δ = 1.62-1.78 (m, 2H), 2.02-2.18 (m, 2H), 2.31-2.37 (m, 1H), 2.40 (s, 3H), 2.50-2.56 (m, 1H), 3.40-3.48 (m, 1H), 5.11 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$/TMS) (ppm): δ = 17.6 (CH_2), 21.5 (Ar-CH_3), 30.8 (CH_2), 34.2 (CH_2), 60.2 (N-CH), 127.1 (Ar-C), 129.7 (Ar-C), 136.1 (Ar-C), 143.8 (Ar-C), 213.2 (C=O). EI-MS *m*/*z* (intensity): 253 (1.20) [M^+], 91 (100) [*p*-Me-Ph^+]. IR (cm^{-1}): 1739 (s, C=O), 3272 (s, NH).

4-methyl-*N*-(2-oxo-cyclohexyl)-benzenesulfonamide (3b):[2] 76% yield; white solid; m.p. 116-118°C; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (ppm): δ = 1.50-1.66 (m, 3H), 1.82-1.85 (m, 1H), 2.03-2.09 (m, 1H), 2.21-2.25 (m, 1H), 2.40 (s, 3H), 2.44-2.55 (m, 2H), 3.74 (m, 1H), 5.78 (d, *J* = 4.5 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$/TMS) (ppm): δ = 21.4 (Ar-CH_3), 23.8 (CH_2), 27.3 (CH_2), 36.7 (CH_2), 40.7 (CH_2), 60.5 (N-CH), 126.9 (Ar-C), 129.6 (Ar-C), 136.8 (Ar-C), 143.5 (Ar-C), 205.7 (C=O) EI-MS *m*/*z* (intensity): 267 (10) [M^+], 91 (100) [p-Me-Ph^+]. IR (cm^{-1}): 1708 (s, C=O), 3276 (s, NH).

***N*-(2-oxo-cyclohexyl)-benzamide (3d):**[3] 80% yield; white solid; m.p. 127-128°C; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (ppm): δ = 1.44 (m, 1H), 1.62-1.95 (m, 3H), 2.21 (m, 1H), 2.41-2.62 (m, 2H), 2.82 (m, 1H), 4.67 (m, 1H), 7.22 (d, *J* = 4.5 Hz, 1H), 7.45 (m, 3H), 7.83 (m, 2H). ^{13}C NMR ($CDCl_3$/TMS) (ppm): δ = 23.9 (CH_2), 28.0 (CH_2), 35.5 (CH_2), 41.1 (CH_2), 58.4 (N-CH), 127.0 (Ar-C), 128.5 (Ar-C), 131.6 (Ar-C), 134.0 (Ar-C), 166.7 (N-C=O), 207.9 (C=O). EI-MS *m*/*z* (intensity): 217 (47.89) [M^+], 105 (100) [$PhCO^+$], 77 (49.75) [Ph^+]. IR (cm^{-1}): 1714 (s, C=O), 1631 (s, C=O), 3259 (s, NH)

***N*-phenacyl-toluene-4-sulfonamide (3e):**[2] 40% yield; white solid; m.p. 110-111°C; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (ppm): δ = 2.39 (s, 3H), 4.46 (d, *J* = 4.5Hz, 2H), 5.65 (s, 1H), 7.27 (d, *J* = 7.8Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$/TMS) (ppm): δ = 21.5 (Ar-CH_3), 48.6 (N-CH_2), 127.1 (Ar-C), 127.9 (Ar-C), 128.9 (Ar-C), 129.8 (Ar-C), 133.6 (Ar-C), 134.4 (Ar-C), 135.9 (Ar-C), 143.7 (Ar-C), 192.4 (C=O). EI-MS *m*/*z* (intensity): 289 (0.31) [M^+], 105 (100)

[$PhCO^+$]. IR (cm^{-1}): 1687 (s, C=O), 3280 (m, NH).

***N*-(1-oxo-indan-2-yl)-4-methyl-benzenesulfonamide (3f):** 55% yield; white solid; m.p. 129-130°C; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (ppm): δ = 2.44 (s, 3H), 3.17 (dd, *J* = 5.4, 5.4 Hz, 1H), 3.65 (dd, *J* = 7.8, 8.1 Hz, 1H), 3.88 (m, 1H), 5.31 (s, 1H), 7.33-7.47 (m, 4H), 7.62-7.74 (m, 2H), 7.84 (dd, *J* = 1.8, 2.1 Hz, 2H). ^{13}C NMR ($CDCl_3$/TMS) (ppm): δ = 21.5 (Ar-CH3), 36.4 (CH2), 58.4 (N-CH), 124.3 (Ar-C), 126.7 (Ar-C), 127.4 (Ar-C), 128.0 (Ar-C), 129.8 (Ar-C), 133.6 (Ar-C), 135.6 (Ar-C), 136.1 (Ar-C), 143.9 (Ar-C), 151.4 (Ar-C), 201.2 (C=O). EI-MS *m*/*z* (intensity):299 (3.91). IR (cm^{-1}): 1722 (s, C=O), 3254 (s, NH). Anal. Calcd for $C_{16}H_{15}NO_3S$: C 63.77, H 5.05, N4.65. Found: C 63.69, H 4.96, N 4.50.

4-methyl-*N*-(2-oxo-1-pentyl-2-methyl-ethyl)-benzenesulfonamide (3g) and 4-methyl-*N*-(2-oxo-1-methyl-2-pentyl-ethyl)-benzenesulfonamide (3g'): 74% Yield; white solid; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (ppm): δ = 0.83 (t, *J* = 8.1 Hz, 3H), 1.08-1.42 (m, 8H), 1.64 (m, 0.74H, $\underline{CH_3}$ of 3g'), 2.04 (s, 2.17H, $\underline{CH_3}$ of 3g), 3.90 (m, 1H), 5.46 (d, *J* = 7.2 Hz, 0.59H, <u>NH</u> of 3g), 5.60 (d, *J* = 7.2 Hz, 0.26H, <u>NH</u> of 3g'), 7.28 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$/TMS) (ppm): δ = 13.73, 13.83 (CH_3), 21.43, 21.45 (Ar-CH_3), 19.05 (CH_2), 22.23, 22.25 (CH_2), 23.06 (CH_2), 24.02 (CH_2), 26.55 (CH_2), 30.98, 31.20 (CH_2), 38.81 (CH_2), 56.94, 61.82 (CH_2), 127.05 (Ar-C), 129.60, 129.63 (Ar-C), 136.69 (Ar-C), 143.52, 143.55 (Ar-C), 205.59 (C=O). Anal. Calcd for $C_{15}H_{23}NO_3S$: C 60.58, H 7.79, N4.71. Found: C 60.46, H 7.64, N 4.76.

***N*-(1-formyl-heptyl)-4-methyl-benzenesulfonamide (3h) and 4-methyl-*N*-(2-oxo-2-hexyl-ethyl) -benzenesulfonamide (3h'):** 20% Yield; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (ppm): δ = 0.86 (t, *J* = 7.2 Hz, 3H), 1.20-1.35 (m, 8H), 1.49 (m, 1.4H, $\underline{CH_2}$CH of 3h), 2.33 (t, *J* = 7.5 Hz, 0.79H, $\underline{CH_2}$CO of 3h'), 2.40 (s, 3H), 3.84 (m, 1H), 5.37 (d, *J* = 6.3 Hz, 0.61H), 7.29 (d, *J* = 6.9 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 9.43 (s, 0.30H). EI-MS *m*/*z* (intensity): 298 (0.61) [M+1], 91 (100) [*p*-Me-Ph^+].

2-[(4-methylphenyl)sulfonyl]amino-propiophenone (3i)[4] **and *N*-(2-oxo-1-phenyl-**

propyl)-4- methyl-benzenesulfonamide (3i')[4]: 82% yield; white solid; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) (ppm): δ = 1.40 (d, *J* = 7.2 Hz, 2.46H, $\underline{CH_3}$ of 3i), 1.99 (s, 0.57H, $\underline{CH_3}$ of 3i'), 2.31, 2.34 (s, 3H), 4.91-5.05 (m, 1H), 5.83 (d, *J* = 8.1 Hz, 0.72H), 6.11 (d, *J* = 4.5 Hz, 0.20H), 7.08-7.78 (m, 9H). ^{13}C NMR ($CDCl_3$/TMS) (ppm): δ = 21.0 (Ar-CH_3), 21.3, 26.7 (CH_3), 53.2, 66.3 (N-CH), 126.9 (Ar-C), 127.0 (Ar-C), 127.9 (Ar-C), 128.4 (Ar-C), 128.5 (Ar-C), 128.7 (Ar-C), 128.9 (Ar-C), 129.2 (Ar-C), 129.6 (Ar-C), 134.0 (Ar-C), 143.4 (Ar-C), 198.0, 202.0 (C=O). EI-MS *m*/*z* (intensity): 91 (100), 260 (8.83).

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