Novel Aziridination of Olefins: Direct Synthesis from Sulfonamides Using *t*-BuOI

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General Methods.

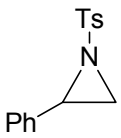
Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained on a Jasco FT/IR-410 infrared spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^{1}H-NMR, 270 MHz; ^{13}C-NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were measured with a Shimadzu Model GCMS-QP5000 spectrometer. High-resolution mass spectral data were obtained on a JEOL DX-303 mass spectrometer. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. Flash column chromatography (FCC) was performed using silica gel FL60D (Fuji Silysia Chemical Co.). Preparative gel permeation liquid chromatography (GPLC) was performed on a JAI (Japan Analytical Industry) LC-908 instrument with JAIGEL 1H-2H columns and chloroform as an eluent. Analytical thin layer chromatography was performed using EM reagent 0.25

mm silica gel 60-F plates. Visualization was accomplished with UV light and spraying with an ethanolic phosphomolybdic acid solution followed by heating.

General Procedure for the synthesis of aziridines.

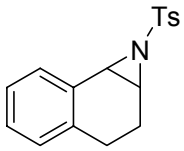
To a mixture of the sulfonamide (0.5 mmol), the olefin (1.0 mmol) and NaI (1.0-1.5 mmol) in MeCN (3 mL) was added *t*-BuOCl (1.0-1.5 mmol). The mixture was allowed to stir in the dark at room temperature for indicated time under an atmosphere of nitrogen, quenched with 0.3M aqueous $Na_2S_2O_3$ (3 mL), extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate).

***N*-(*p*-Toluenesulfonyl)-2-phenylaziridine (1)**.



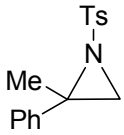
According to the above general procedure, *p*-toluenesulfonamide (86 mg, 0.50 mmol) and styrene (105 mg, 1.01 mmol) were used, and the title compound was isolated (130 mg, 95%). Spectroscopic data were in agreement with those for the previously reported material.[1] White solid; mp 64-67 °C; TLC R_f 0.37 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.38 (d, 1H, *J* = 4.6 Hz, -NC*H*HCH-), 2.43 (s, 3H, ArCH_3), 2.98 (d, 1H, *J* = 7.3 Hz, -NCH*H*CH-), 3.77 (dd, 1H, *J* = 4.6, 7.3 Hz, -CH_2C*H*N-), 7.19-7.36 (m, 7H, Ar*H*), 7.86 (d, 2H, *J* = 8.2 Hz, Ar*H*).

***N*-(*p*-Toluenesulfonyl)amino-1,2,3,4-tetrahydronapthalene-1,2-imine.**



According to the above general procedure, *p*-toluenesulfonamide (85 mg, 0.50 mmol) and 1,2-dihydronaphtalene (131 mg, 1.00 mmol) were used, and the title compound was isolated (114 mg, 76%). Spectroscopic data were in agreement with those for the previously reported material.[1] Colorless crystalline solid; mp 123-126 °C; TLC R_f 0.27 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.66 (ddd, 1H, *J* = 5.4, 13.8, 13.9 Hz, -NCHC*H*HCH$_2$-), 2.24 (ddt, *J* = 2.3, 5.9, 13.9 Hz, -NCHCH*H*CH$_2$-), 2.40 (s, 3H, ArC*H*$_3$), 2.52 (dd, 1H, *J* = 5.9, 14.9 Hz, -NCHCH$_2$C*H*H-), 2.75 (ddd, 1H, *J* = 5.9, 13.8, 14.9 Hz, -NCHCH$_2$CH*H*-), 3.55 (dt, 1H, *J* = 2.3, 7.0 Hz, -NC*H*CH$_2$-), 3.81 (d, *J* = 7.0 Hz, -NC*H*CHCH$_2$-), 7.02-7.30 (m, 6H, Ar*H*), 7.81 (d, 2H, *J* = 8.1 Hz, Ar*H*).

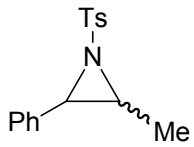
***N*-(*p*-Toluenesulfonyl)-2-methyl-2-phenylaziridine**



A mixture of *p*-toluenesulfonamide (86 mg, 0.50 mmol), α-methylstyrene (114 mg, 0.97 mmol), NaI (225 mg, 1.50 mmol), and *t*-BuOCl (166 mg, 1.53 mmol) in MeCN (3 mL) was stirred at room temperature for 2 h, quenched with 0.3M aqueous $Na_2S_2O_3$ (3 mL), extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated under vacuum. Analysis of the crude product by ^{1}H-NMR revealed that the aziridine was formed in 81% ^{1}H-NMR yield. The residue was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 9/1) to afford 74 mg (52%) of the aziridine. Spectroscopic data were in agreement with those for the previously reported material.[1] Colorless oil; TLC R_f 0.33 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.05 (s, 3H, -NCH$_2$CC*H*$_3$(Ph)-),

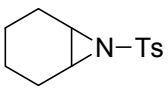
2.43 (s, 3H, $ArCH_3$), 2.52 (s, 1H, -NC*H*HCH_3(Ph)-), 2.96 (s, 1H, -NCH*H*CH_3(Ph)-), 7.25-7.39 (m, 7H, Ar*H*), 7.87 (d, 2H, *J* = 8.4 Hz, Ar*H*).

cis- and _trans_-_N_-(_p_-Toluenesulfonyl)-2-methyl-3-phenylaziridine



According to the above general procedure, *p*-toluenesulfonamide (86 mg, 0.50 mmol) and *cis*-β-methylstyrene (119 mg, 1.00 mmol) were used, and the title compound was isolated (96 mg, 66%, *cis* / *trans* = 41 / 59) as a mixture of the *cis* and *trans*-aziridine. Spectroscopic data were in agreement with those for the previously reported material.[1] Colorless crystalline solid; TLC R_f 0.33 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.02 (d, 3H, *J* = 5.7 Hz, -CHC*H*$_3$, *cis*), 1.84 (d, 3H, *J* = 6.1 Hz, -CHC*H*$_3$, *trans*), 2.38 (s, 3H, ArC*H*$_3$, *trans*), 2.43 (s, 3H, ArC*H*$_3$, *cis*), 2.91 (dq, 1H, *J* = 4.3, 6.1 Hz, -NC*H*(CH_3)CH(Ph)-, *trans*), 3.18 (dq, 1H, *J* = 5.7, 7.2 Hz, -NC*H*(CH_3)CH(Ph)-, *cis*), 3.78 (d, 1H, *J* = 4.3 Hz, -CH(CH_3)-C*H*(Ph)N-, *trans*), 3.92 (d, 1H, *J* = 7.2 Hz, -CH(CH_3)-C*H*(Ph)N-, *cis*), 7.12-7.31 (m, 7H, Ar*H*, *cis* and *trans*), 7.82 (d, 2H, *J* = 8.4 Hz, Ar*H*, *trans*), 7.88 (d, 2H, *J* = 8.4 Hz, Ar*H*, *cis*).

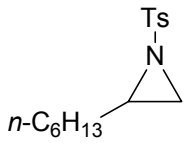
7-(_p_-Toluenesulfonyl)-7-azabicyclo[4.1.0]heptane.



According to the above general procedure, *p*-toluenesulfonamide (85 mg, 0.50 mmol) and cyclohexene (81 mg, 0.99 mmol) were used, and the title compound was isolated (72 mg, 58%). Spectroscopic data were in agreement with those for the previously reported material.[1] Colorless

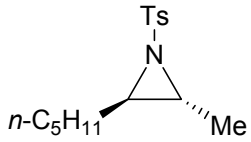
crystalline solid; mp 50-53 °C; TLC R_f 0.23 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.14-1.21 (m, 2H, -CH_2C*H*HC*H*HCH_2-), 1.25-1.47 (m, 2H, -CH_2CH*H*CH*H*CH_2-), 1.79 (dt, 4H, *J* = 1.4, 5.8 Hz, -CHC*H*$_2$$CH_2$$CH_2$C*H*$_2$CH-), 2.44 (s, 3H, ArC*H*$_3$), 2.97 (t, 2H, *J* = 1.4 Hz, -NC*H*C*H*N-), 7.32 (d, 2H, *J* = 8.1 Hz, Ar*H*), 7.81 (d, 2H, *J* = 8.1 Hz, Ar*H*).

***N*-(*p*-Toluenesulfonyl)-2-hexylaziridine.**



According to the above general procedure, *p*-toluenesulfonamide (86 mg, 0.50 mmol) and 1-octene (114 mg, 1.02 mmol) were used, and the title compound was isolated (108 mg, 77%). Spectroscopic data were in agreement with those for the previously reported material.[1] Colorless oil; TLC R_f 0.29 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.85 (t, 3H, *J* = 6.8 Hz, -CH_2C*H*$_3$), 1.18-1.37 (m, 9H, -CHC*H*HC*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$$CH_3$), 1.51-1.58 (m, 1H, -CHCH*H*CH_2-), 2.06 (d, 1H, *J* = 4.6 Hz, -NC*H*HCH-), 2.44 (s, 3H, ArC*H*$_3$), 2.64 (d, 1H, *J* = 7.0 Hz, -NCH*H*CH-), 2.66-2.71 (m, 1H, -NCH_2C*H*N-), 7.33 (d, 2H, *J* = 8.4 Hz, Ar*H*), 7.82 (d, 2H, *J* = 8.4 Hz, Ar*H*).

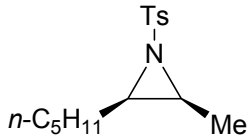
***trans*-*N*-(*p*-Toluenesulfonyl)-2-methyl-3-pentylaziridine.**



According to the above general procedure, *p*-toluenesulfonamide (86 mg, 0.50 mmol) and *trans*-2-octene (117 mg, 1.05 mmol) were used, and the title compound was isolated (90 mg, 63%). Spectroscopic data were in agreement with those for the previously reported material.[2] Colorless oil; TLC R_f 0.33

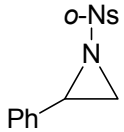
(hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.82 (t, 3H, J = 6.5 Hz, CH_3CH$_2$-), 1.11-1.26 (m, 6H, CH$_3$CH_2CH$_2$-CH_2CH$_2$CH-), 1.41-1.66 (m, 2H, -CH$_2$CH_2CHCHCH$_3$), 1.55 (d, 3H, J = 5.4 Hz, -CHCH_3), 2.43 (s, 3H, ArCH_3), 2.65-2.71 (m, 2H, -NCH(CH$_3$)CHN-), 7.31 (d, 2H, J = 8.4 Hz, ArH), 7.83 (d, 2H, J = 8.4 Hz, ArH).

***cis*-*N*-(*p*-Toluenesulfonyl)-2-methyl-3-pentylaziridine.**



According to the above general procedure, *p*-toluenesulfonamide (85 mg, 0.50 mmol) and *cis*-2-octene (110 mg, 0.98 mmol) were used, and the title compound was isolated (115 mg, 82%). Spectroscopic data were in agreement with those for the previously reported material.[2] Colorless oil; TLC R_f 0.37 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.83 (t, 3H, J = 6.5 Hz, CH_3CH$_2$-), 1.10-1.25 (m, 9H, CH$_3$CH_2CH_2CH-$_2$CH$_2$CHCHCH_3), 1.27-1.50 (m, 2H, -CH$_2$CH_2CH-), 2.44 (s, 3H, ArCH_3), 2.69-2.76 (dq, 1H, J = 6.3, 6.4 Hz, -NCH(CH$_3$)CH-) 2.88-2.97 (dt, 1H, J = 6.3, 6.6 Hz, -CH(CH$_3$)CHN-), 7.32 (d, 2H, J = 8.1 Hz, ArH), 7.82 (d, 2H, J = 8.1 Hz, ArH).

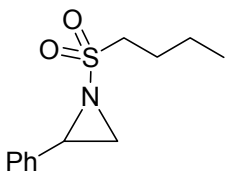
***N*-(2-Nitrobenzenesulfonyl)-2-phenylaziridine**.



According to the above general procedure, 2-nitrobenzenesulfonamide (101 mg, 0.50 mmol) and styrene (104 mg, 1.00 mmol) were used, and the title compound was isolated (102 mg, 66%). Spectroscopic data were in agreement with those for the previously reported material.[3] Pale yellow oil; TLC R_f 0.07 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.63 (d, 1H, J = 4.7 Hz, -NCHHCH-), 3.24 (d, 1H, J = 7.2 Hz, -NCHHCH-), 4.03 (dd, 1H, J

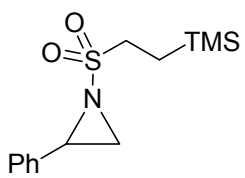
= 4.7, 7.2 Hz, -NCH$_2$C*H*N-), 7.25-7.34 (m, 5H, Ar*H*), 7.69-7.78 (m, 3H, Ar*H*), 8.21-8.25 (m, 1H, Ar*H*).

***N*-(1-Butanesulfonyl)-2-phenylaziridine.**



According to the above general procedure, *n*-butanesulfonamide (69 mg, 0.50 mmol) and styrene (107 mg, 1.03 mmol) were used, and the title compound was isolated (110 mg, 92%). Colorless oil; TLC R_f 0.29 (hexane/EtOAc, 4:1); IR (neat, cm^{-1}) 2962, 1606, 1498, 1323, 1149; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.92 (t, 3H, *J* = 7.4 Hz, -CH$_2$C*H$_3$*), 1.46 (tq, 2H, *J* = 7.4, 7.6 Hz, -CH$_2$C*H$_2$*CH$_3$), 1.89 (tt, 2H, *J* = 7.6, 7.9 Hz, -SO$_2$CH$_2$C*H$_2$*CH$_2$-), 2.40 (d, 1H, *J* = 4.5 Hz, -NC*H*HCHN-), 2.97 (d, 1H, *J* = 7.2 Hz, -NCH*H*CHN-), 3.18 (t, 2H, *J* = 7.9 Hz, -SO$_2$C*H$_2$*CH$_2$-), 3.69 (dd, 2H, *J* = 4.5, 7.2 Hz, -NCH$_2$C*H*N-), 7.26-7.38 (m, 5H, Ar*H*); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 13.3, 21.4, 24.8, 35.0, 40.4, 52.2, 126.3, 128.3, 128.5, 134.9; MS (EI) *m/z* (relative intensity, %) 239 (M^+, 1), 118 (M^+–*n*-BuSO$_2$, 93), 91 (100); Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85. Found: C, 60.22; H, 7.18; N, 5.76.

***N*-[2-(Trimethylsilyl)ethanesulfonyl]-2-phenylaziridine**.



According to the above general procedure, 2-(trimethylsilyl)-ethanesulfonamide (91 mg, 0.50 mmol) and styrene (105 mg, 1.01 mmol) were used, and the title compound was isolated (138 mg, 97%). Spectroscopic data were in agreement with those for the previously reported material.[4] Colorless oil; TLC R_f 0.36 (hexane/EtOAc, 4:1); ^{1}H NMR ($CDCl_3$, 270

MHz) δ 0.03 [s, 9H, -Si(C*H*$_3$)$_3$], 1.07-1.14 (m, 2H, -CH$_2$C*H*$_2$TMS), 2.40 (d, 1H, *J* = 4.3 Hz, -NC*H*HCHN-), 2.95 (d, 1H, *J* = 7.2 Hz, -NCH*H*CHN-), 3.06-3.13 (m, 2H, -SO$_2$C*H*$_2$CH$_2$TMS), 3.67 (dd, 1H, *J* = 4.3, 7.2 Hz, -NC*H*CH$_2$N-), 7.23-7.37 (m, 5H, Ar*H*).

References

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2 T. Ando, D. Kano, S. Minakata, I. Ryu and M. Komatsu, *Tetrahedron* 1998, **54**, 13485-13494.

3 S. K. Kim and E. N. Jacobsen, *Angew. Chem., Int. Ed.* 2004, **43**, 3952-3954.

4 P. Dauban and R. H. Dodd, *J. Org. Chem*. 1999, **64**, 5304-5307.