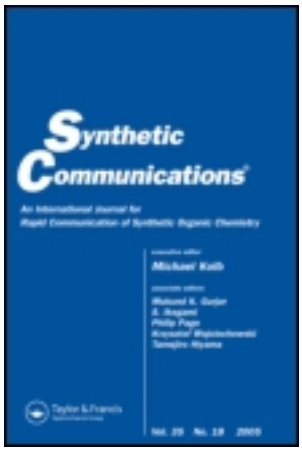

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Synthesis of Functionalized *N*-Arylsulfonyl Aziridines from α,β-Unsaturated Esters, Amides, Ketones, and Nitriles Using *N*,*N*-Dichloroarylsulfonamides as Nitrogen Source

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ABSTRACT

A convenient and general aziridination process has been developed for the synthesis of functionalized *N*-arylsulfonylaziridines bearing an alkoxycarbonyl, acyl, cyano, and carboxamide group at C_2. The two-step sequence involves addition of *N*,*N*-dichloroarylsulfonamide to the appropriate olefin in the presence of $Cu(acac)_2$, treatment of the resultant chlorosulfonamide with Na_2SO_3, followed by cyclization with NaOH to give the appropriate aziridine in good yields. The reaction is found to be an anti-stereoselective.

Key Words: Aziridination; *N*-Arylsulfonyl aziridine; *p*-Toluenesulfonamide; Alkenes.

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1. INTRODUCTION

Aziridines are important precursors for the synthesis of alkaloids, amino-acids, aminosugars, and β-lactams[1] and have been used as ligands in metal catalyzed asymmetric transformations.[2] *N*-Arylsulfonylaziridines have recently attracted attention due to their susceptibility towards nucleophilic ring opening and ring expansion reactions.[3]

We have been interested in exploring various synthetic uses of *N*-arylsulfonylaziridines and have employed them to access azetidines[4] and imidazolidinones[5] (for eventual conversion to enantiomerically pure diamines and diaminoacids). So we were looking for a convenient and cost-effective procedure for the preparation of functionalized *N*-arylsulfonylaziridines. An attractive route to aziridines could involve a single atom transfer to double bonds.[6] (For epoxidation see Ref. [6c].) But carbene addition to imines[7] and reaction of thermally or photochemically generated nitrenes with olefins[8] suffer from poor yields and formation of side products. Transition metal catalyzed addition of nitrenes generated from [*N*-(arenesulfonyl)-imino] phenyliodinanes[9,10](PhI = NSO_2Ar) to olefins have been more successful. However, PhI = NSO_2Ar is expensive and unstable and the procedure is inconvenient[11] because it yields beside aziridines, iodobenzene and oxygenated hydrocarbons as substantial by-products. Several literature reports have described[12] the use of chloramine-T (*N*-chloro-*N*-sodio-*p*-toluenesulfonamide) as nitrene source for the aziridination of alkenes but these reactions fail in the case of electron deficient α,β-unsaturated olefins.[13] To the best of our knowledge, there are no references on the synthesis of functionalized aziridines based on dichloramine-T till date. We now report this synthetic transformation through a two step sequence involving addition of *N*,*N*-dichloroarylsulfonamide to the α,β-unsaturated olefins in the presence of $Cu(acac)_2$, followed by cyclization with NaOH.

2. RESULTS

Although the aziridination of electron-deficient olefins using PhI = NTs and Cu(II) catalyst has been reported, the method suffers from the following restrictions.

(1) Costly reagents and catalysts; (2) inconvenience in handling reagents and catalysts; (3) poor yields.

In view of above limitations these reactions were investigated with dichloramine-T using transition metal catalyzed addition of *N*-arylsulfonyl group to functionalized α,β-unsaturated olefins by using *N*,*N*-dichloroarylsulfonamide as nitrogen source and a Cu(II) catalyst.

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We have previously prepared *N*-arylsulfonylaziridines by addition of *N*,*N*-dichloroarylsulfonamides to the appropriate olefin, followed by cleavage of the N–Cl bond with $NaHSO_3$ and cyclization with a base.[14] However, the procedure did not work when the olefin had a functional group like –CN, –COOR, –COR, or $-CONH_2$ on it, since addition of dichloramine-T to the olefin was unsuccessful.[15] Recently Li et al.[16] have reported somewhat similar addition to α,β-unsaturated esters to prepare amino halogenated product. We followed similar procedure using $Cu(acac)_2$ as catalyst instead of $Cu(OTf)_2$ to synthesize amino chlorinated products and then cyclized these amino chlorinated products using a base to get the corresponding aziridines.

The *N*,*N*-dichloro-*p*-toluenesulfonamide ($TsNCl_2$) employed in this sequence was prepared by the treatment of *p*-toluenesulfonamide with commercial bleaching powder, followed by CH_3COOH acidification.[14c,17] Both $Cu(OTf)_2$ and $Cu(acac)_2$ were tried for the reaction and we found that yields are comparable in both cases. Therefore, we chose $Cu(acac)_2$ as the catalyst because it is less costly and easy to handle.

For cyclization several bases in different solvents were tried, e.g., NaOH–aq. EtOH, NaOH–aq. MeOH, NaH–THF but best results were obtained with NaOH in aq. THF.

In some cases (entries **1g**, **1i**, **1j**; Table 1), more concentrated NaOH solution was required, whereas the sulfonamide corresponding to entry **1a** and **1b** decomposed by a higher concentration of the base. The reaction was generalized by reacting a variety of electron-deficient α,β-unsaturated olefins with

Table 1. Metal catalyzed aziridination of olefins using *N*,*N*-dichloro-*p*-toluenesulfonamide.

Substrate	R_1	R_2	R_3	EWG	Ref. of Product	Product (yield %)[b]
1a	H	H	H	CO_2Me	[9c]	**2a** (80)
1b	Ph	H	H	CO_2Me	[9c]	**2b** (76)
1c[a]	$Cl-C_6H_4$	H	H	CO_2Me	[18]	**2c** (55)
1d[a]	$NO_2-C_6H_4$	H	H	CO_2Me	—	**2d** (68)
1e	CH_3	CH3	H	CO_2Me	[19]	**2e** (60)
1f	Ph	H	H	COMe	[19]	**2f** (70)
1g[a]	$Cl-C_6H_4$	H	H	COPh	[20]	**2g** (60)
1h	H	H	H	CN	[21]	**2h** (52)
1i	Ph	H	H	CN	[21]	**2i** (60)
1j	H	H	H	$CONH_2$	[22]	**2j** (75)

[a]The reaction needed 2 eqiuv. of $TsNCl_2$ and 36–48 hr.
[b]Isolated yield.

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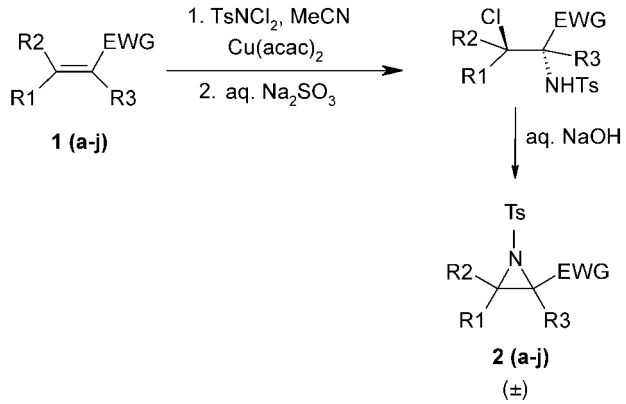
N,*N*-dichloro-*p*-toluenesulfonamide using $Cu(acac)_2$ as catalyst. The reaction sequence is represented in Sch. 1 with the results summarized in Table 1. In all cases reported in Table 1, only trans-isomer was observed by ^1H NMR analysis of the crude products,[a] therefore the reaction seems to be stereoselective.[16] Olefins, bearing electron-withdrawing groups like chloro or nitro on the phenyl ring (entries **1c**, **1d**, and **1g**) needed 2 equiv. of dichloramine-T and greater reaction time for best results. All these reactions were associated with the formation of *p*-toluenesulfonamide as by-product along with the aziridine.

We also examined some dichloramine-T analogs in the aziridination reaction. The aziridination of methyl acrylate using dichloramine-B, which contains no substituents on the benzene ring, as nitrogen source afforded the corresponding aziridine in 65% yield. Similarly *p*-chloro substituted analog also reacted with methyl acrylate to give aziridine in 50% yield.

To compare the efficiency of the present method with Evan's method for functionalized aziridines we have listed in Table 2 yields of some aziridines using same catalyst, i.e., $Cu(acac)_2$.

3. CONCLUSION

In conclusion, we have developed a cost-effective and general method for the synthesis of functionalized *N*-arylsulfonylaziridines in good yields. The reaction is performed easily at room temperature and requires a relatively cheaper copper complex, $Cu(acac)_2$ as catalyst. The possibility of developing it into an asymmetric aziridination process is being explored.



Scheme 1. Electron withdrawing groups (EWG) = COOMe, COR, CN, $CONH_2$.

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Table 2. Comparison of yields of some functionalized aziridines with present and Evan's method.

			Yield (%)	
Entry	Aziridines	Cu(II) catalyst	Evan's	Present
1	**2a**	$Cu(acac)_2$	32	80
2	**2b**	$Cu(acac)_2$	36	76
3	**2e**	$Cu(CH_3CN)_4ClO_4$	38	60
4	**2f**	$Cu(acac)_2$	56	70

4. EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a DPX-300 Brucker spectrometer. Data are reported as follows: Integration, chemical shift in parts per million (ppm) from tetramethylsilane (TMS) on the δ scale, multiplicity (s = singlet, d = doublet, t = triplet, dd = double doublet, and m = multiplet), coupling constant in Hertz (Hz), and assignment. Melting points were determined using a ELECTRON-Bombay micro melting point apparatus and are uncorrected. IR absorption spectra were recorded on Nicolet 5DX FTIR instrument and values are reported in cm^{-1}. Monitoring of the reactions was performed using silica gel TLC plates (silica Merck 60 F_{254}). Spots were visualized by UV light at 254 nm. Column chromatography was performed using silica gel (60–120 mesh). Organic solvents were purified by standard procedures.

4.1. General Procedure for Aziridination of Functionalized α,β-Unsaturated Olefins by *N*,*N*-Dichloroarylsulfonamides

Into a dry round-bottom flask was added functionalized α,β-unsaturated olefin (0.74 mmol) and freshly distilled acetonitrile (2.5 mL). The contents were stirred at room temperature and 4 Å molecular sieves (220 mg), $TsNCl_2$ (0.89 mmol, 1.20 equiv.), and $Cu(acac)_2$ (8 mol%) were added. The resulting solution was stirred at room temperature for 24 hr. Saturated aqueous Na_2SO_3 solution (3 mL) was added dropwise at the end of the reaction. Two phases were separated and the aqueous phase extracted with ethylacetate (3 × 15 mL). The combined organic layers were washed with 10% aqueous ammonia and brine, dried over anhydrous sodium sulfate, and concentrated to dryness. The resultant solid was purified by crystallization (benzene–pet. ether) to give the corresponding sulfonamide. To a solution of the above sulfonamide in THF was added dropwise 10% aqueous sodium hydroxide solution in THF.

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This mixture was stirred (15–20 mins) at room temperature. Completion of the reaction was checked by TLC. The reaction mixture was extracted with ethylacetate (3 × 10 mL) and washed with water (3 × 10 mL) and dried over anhydrous Na_2SO_4. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc) to give the corresponding aziridine.

***N*-(*p*-Toluensulfonyl)-2-methoxycarbonyl aziridine (2a).** Colorless oil (lit.,[10c] colorless oil); ν_{max} (cm^{-1}) 1748 (CO), 1332 and 1163 (SO_2) cm^{-1}; δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.84 (2H, d, *J* 8.3, Ar-H), 7.36 (2H, d, *J* 8.2, Ar-H), 3.74 (3H, s, OCH_3), 3.34 (1H, dd, *J* 7.1, 4.1, $CHCO_2Me$), 2.76 (1H, d, *J* 7.2, *cis*-CH), 2.56 (1H, d, *J* 4.1, *trans*-CH), 2.45 (3H, s, Ar-CH_3); δ_C (75 MHz, $CDCl_3$, Me_4Si) 167.1, 145.2, 133.9, 129.8, 128.1, 52.7, 35.6, 31.9, 21.5.

***trans*-*N*-(*p*-Toluenesulfonyl)-2-methoxycarbonyl-3-phenylaziridine (2b).** White crystalline solid, m.p. 44–45°C (lit.,[10c] 44.2–44.6°C); ν_{max} (cm^{-1}) 1752 (CO), 1335 and 1165 (SO_2); δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.77 (2H, d, *J* 8.3, Ar-H), 7.31–7.24 (7H, m, Ar-H), 4.44 (1H, d, *J* 3.9, C–H), 3.85 (s, 3H, s, OCH_3), 3.53 (1H, d, *J* 4.0, C–H), 2.41 (3H, s, Ar-CH_3); δ_C (75 MHz, $CDCl_3$, Me_4Si) 166.2, 144.3, 136.9, 132.5, 129.5, 128.9, 128.5, 127.4, 127.3, 53.1, 47.6, 46.7, 21.6.

***N*-(*p*-Toluenesulfonyl)-2-methoxycarbonyl-3-(*p*-chlorophenyl) aziridine (2c).** Solid, m.p. 110°C; ν_{max} (cm^{-1}) 1742 (CO), 1328 and 1162 (SO_2); δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.71 (2H, d, *J* 8.2, Ar-H), 7.31–7.24 (6H, m, Ar-H), 4.39 (1H, d, *J* 3.9, C–H), 3.78 (3H, s, OCH_3), 3.49 (1H, d, *J* 3.9, C–H), 2.43 (3H, s, Ar-CH_3); δ_C (75 MHz, $CDCl_3$, Me_4Si) 165.5, 144.5, 136.5, 134.6, 131.0, 129.6, 128.7, 127.8, 127.4, 53.2, 47.9, 45.5, 21.6.

***N*-(*p*-Toluenesulfonyl)-2-methoxycarbonyl-3-(*p*-nitrophenyl) aziridine (2d).** Solid, m.p. 132–135°C (Found: C, 54.04; H, 4.26; N, 7.26. $C_{17}H_{16}N_2O_6S$ requires C, 54.25; H, 4.28; N, 7.44%); ν_{max} (cm^{-1}) 1758 (CO), 1376 and 1163 (SO_2), 1543 (NO_2); δ_H (300 MHz, $CDCl_3$, Me_4Si) 8.16 (2H, d, *J* 8.7, Ar-H), 7.80 (2H, d, *J* 8.2, Ar-H), 7.43 (2H, d, *J* 8.6, Ar-H), 7.33 (2H, d, *J* 6.6, Ar-H), 4.53 (1H, d, *J* 3.6, C–H), 3.88 (3H, s, OCH_3), 3.51 (1H, d, *J* 3.5, C–H), 2.44 (3H, s, Ar-CH_3); δ_C (75 MHz $CDCl_3$ Me_4Si) 165.4, 148.1, 144.9, 140.0, 136.4, 134.6, 129.7, 128.1, 127.4, 123.8, 53.3, 47.5, 45.9, 21.6.

Methyl 3,3-dimethyl-*N*-(*p*-toluenesulfonyl) aziridine-2-carboxylate (2e). Viscous oil; ν_{max} (cm^{-1}) 1738 (CO), 1335 and 1165 (SO_2); δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.86 (2H, d, *J* 8.1, Ar-H), 7.32 (2H, d, *J* 8.1, Ar-H), 3.70 (3H, s, OCH_3), 3.51 (1H, s, C–H), 2.44 (3H, s, Ar-CH_3), 1.83 (3H, s), 1.39 (3H, s); δ_C (75 MHz, $CDCl_3$, Me_4Si) 166.7, 144.1, 137.2, 129.5, 127.2, 52.3, 52.2, 48.7, 21.5, 21.3, 20.7.

***trans*-2-Acetyl-3-phenyl-*N*-(*p*-toluenesulfonyl) aziridine (2f).** ν_{max} (cm^{-1}) 1680 (CO), 1335 and 1165 (SO_2); δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.93 (2H, d, *J* 8.1, Ar-H), 7.55–7.24 (7H, m, Ar-H), 4.16 (1H, d, *J* 7.8, C–H), 3.62 (1H, d, *J* 7.9, C–H), 2.47 (3H, s, Ar-CH_3), 1.74 (3H, s,); δ_C (75 MHz,

$CDCl_3$, Me_4Si) 200.3, 144.3, 136.4, 131.5, 129.5, 128.9, 128.3, 127.9, 127.3, 50.9, 48.5, 28.4, 21.4.

***trans*-2-Benzoyl-3-(*p*-chlorophenyl-*N*-(*p*-toluenesulfonyl) aziridine (2g).** Solid, m.p. 148–149.5°C (lit.,[22] 149–150°C); ν_{max} (cm^{-1}) 1696 (CO), 1330 and 1161 (SO_2); δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.98 (2H, d, *J* 8.1, Ar-H), 7.65 (7H, m, Ar-H), 4.16 (1H, d, *J* 7.8, C–H), 3.62 (1H, d, *J* 7.9, C–H), 2.47 (3H, s, Ar-CH_3), 1.74 (3H, s); δ_C (75 MHz, $CDCl_3$, Me_4Si) 200.3, 144.3, 136.4, 131.5, 129.5, 128.9, 128.3, 127.9, 127.3, 50.9, 48.5, 28.4, 21.4.

***N*-(*p*-toluenesulfonyl) aziridine-2-carboxamide (2h).** Waxy solid; ν_{max} (cm^{-1}) 3408 and 3370 (NH_2), 1674 (CO), 1338 and 1164 $\nu(SO_2)$; δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.75 (2H, d, *J* 8.0, Ar-H), 7.30 (2H, d, *J* 7.9, Ar-H), 3.17 (1H, dd, *J* 7.3 and 4.0), 2.74 (1H, d, *J* 7.6), 2.37 (1H, d, *J* 4.1), 2.40 (3H, s, Ar-CH_3).

2-Cyano-*N*-(*p*-toluenesulfonyl)aziridine (2i). Oil; ν_{max} (cm^{-1}) 2218 (CN), 1338 and 1164 (SO_2); δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.8 (2H, d, *J* 7.9), 7.41(2 H, d, *J* 2), 3.23 (1H, dd), 2.89 (1H, d, *J* 7.0), 2.66 (1H, d, *J* 3.6), 2.48 (3H, s, Ar-CH_3); δ_C (75 MHz, $CDCl_3$, Me_4Si) 146.1, 133.05, 130.15, 128.22, 115.03, 32.11, 23.43, 21.73.

2-Cyano-3-phenyl-*N*-(*p*-toluenesulfonyl)aziridine (2j). ν_{max} (cm^{-1}) 2260 (CN), 1339 and 1165 (SO_2); δ_H (300 MHz, $CDCl_3$, Me_4Si) 7.9 (2H, d, *J* 7.9), 7.31 (7H, m), 4.32 (1H, d), 3.06 (1H, d), 2.48 (3H, s); δ_C (75 MHz, $CDCl_3$, Me_4Si) 146.6, 134.3, 133.01, 130.9, 130.01, 129.03, 129.01, 127.01, 114.01, 46.02, 32.01, 22.04.

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NOTE

a. All products (reported in Table 1) are known in literature (except **2d**).

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