(Heteroarylchloromethyl)lithiums as Darzens Reagents: Synthesis of Heteroarylaziridines§

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Like oxiranes, aziridines are highly strained compounds.[1] The ring strain makes them susceptible to ring-opening reactions that dominate their chemistry and give them the ability to act as useful synthetic intermediates for the preparation of a great variety of organic compounds, such as alkaloids,[2] amino acids,[3] aminosugars,[4] antibiotics,[5] aminophosphonic acids,[6] homoallylic amines,[7] labeled propynylglycine,[8] (tosylamino)carbonyl compounds,[9] and pyrrolidines.[10]

There is a wealth of reported synthetic procedures for aziridines, many from alkenes.[11] Aziridines have also been obtained from metalated simpler aziridines,[12] by addition of α-halosulfonyl carbanions,[13] lithiated (chloromethyl)phosphonamides,[6] and α-halo enolates[14] to imines. In view of the above history,[15] we were surprised that the preparation of (heteroaryl)aziridines had not been pursued at all. We now describe the first preparation of a number of (heteroaryl)aziridines based on the lithiation of some heteroarylchloromethanes and subsequent reaction with imines.

Lithiation of 2-(chloromethyl)pyridine (**1a**) (Chart 1) with lithium diisopropylamide (LDA) at −78 °C in tetrahydrofuran produced the dark brown solution of (2-pyridylchloromethyl)lithium (**1b**).[16] Addition of cyclohexylideneaniline (**2a**) (Chart 2) to the solution of **1b** gave a high yield of pyridylaziridine **3a** (Chart 3). Similarly, treatment of **1b** with cyclopentylidene- (**2b**), fluorenylidene- (**2c**), and benzylideneaniline (**2d**) furnished aziridines **3b**, **3c**, and **3d**, respectively. Alkyl and aryl other than cycloalkyl groups are tolerated as substituents in the Schiff's base. Indeed, imines **2f** and **2g** also reacted with **1b** leading to aziridines **3f** and **3g**, respectively. The aziridination works well also for the synthesis of unactivated aziridine **3e** from **1b** and benzylidenebenzenesulfonamide (**2e**).[17] We believe that the aziridine formation is the result of a Darzens-type reaction between **1b** and the imine (Scheme 1).

It is worth noting that the reaction of **1b** with unsymmetrically substituted imines proceeded in a diastereo-

Chart 1

RCHClR[1]

1a: R = 2-Pyridyl; R^1 = H

1b: R = 2-Pyridyl; R^1 = Li

1c: R = 2-Quinolyl; R^1 = H

1d: R = 2-Quinolyl; R^1 = Li

1e: R = 2-Benzothiazolyl; R^1 = H

1f: R = 2-Benzothiazolyl; R^1 = Li

Chart 2

RN=CR[1]R[2]

2a: R = Ph; R^1, R^2 =

2b: R = Ph; R^1, R^2 =

2c: R = Ph; R^1, R^2 =

2d: R = R^2 = Ph; R^1 = H

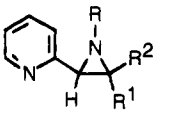
2e: R = SO_2Ph; R^1 = H, R^2 = Ph

2f: R = Ph; R^1 = R^2 = Me

2g: R = R^1 = Ph; R^2 = Me

2h: R = Bz; R^1 = H; R^2 = Ph

Chart 3



3a: R = Ph; R^1, R^2 =

3b: R = Ph; R^1, R^2 =

3c: R = Ph; R^1, R^2 =

3d: R = Ph; R^1 = H, Ra = Ph

3e: R = SO_2Ph; R^1 = H, R^2 = Ph

3f: R = Ph; R^1 = R^2 = Me

3g: R = R^1 = Ph; R^2 = Me

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Scheme 1

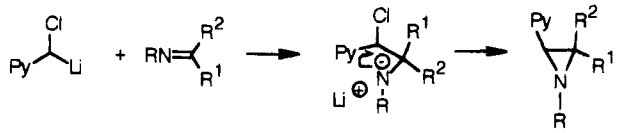
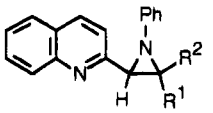


Chart 4



4a: R^1, R^2 = 

4b: $R^1 = R^2$ = Me

4c: R^1 = Me; R^2 = Ph;

Table 1. Reaction of Imines 2a-h with (Pyridylchloromethyl)lithium (1b), (Quinolylchloromethyl)lithium (1d), and (Benzothiazolylchloromethyl)lithium (1f) in THF at −78 °C under Nitrogen

RCHClR[1]	imine[e]	reaction product (% yield)[a]
1b	**2a**	**3a** (73)
1b	**2b**	**3b** (70)
1b	**2c**	**3c** (65)
1b	**2d**	**3d** (72)
1b	**2e**	**3e** (78)
1d	**2a**	**4a** (68)
1d	**2f**	**4b** (40)
1d	**2g**	**4c** (20)
1f	**2a**	**5a** (85)
1f	**2b**	**5b** (70)
1f	**2c**	**5c** (75)
1f	**2d**	**5d** (75)[b]
1f	**2e**	**5e** (60)[c]
1f	**2f**	**5f** (65)
1f	**2g**	**5g** (30)
1f	**2h**	**5h** (77)[d]

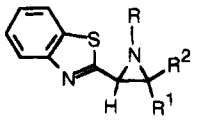
[a] Yields, not optimized, were calculated on isolated and purified compounds. [b] The ^{1}H NMR spectrum of the crude aziridine before purification by crystallization clearly indicates the presence of both the two isomers *E* and *Z* (*E*/*Z* = 4/a). **5d** cis: (90 MHz, $CDCl_3$) δ 3.30−3.65 (dd, 2H, J = 7.0 Hz), 7.10−8.30 (m, 14H). [c] The *E* and *Z* isomeric aziridines have been isolated. See Experimental Section. [d] The *E* and *Z* isomers (*E*/*Z* = 9/1) could not be isolated; the ratio was established by ^{1}H NMR (see Experimental Section). [e] Imines were prepared according to the procedure reported in ref 22.

selective way. Indeed, the reaction of **1b** with imines **2d** and **2e** gave rise to the formation of aziridines **3d** and **3e**, respectively, having *E* configuration.[18]

In analogy with (2-pyridylchloromethyl)lithium (**1b**), (2-quinolylchloromethyl)lithium (**1d**), prepared by lithiation of (2-chloromethyl)quinoline (**1c**), furnished aziridines **4a, 4b**, and **4c** (Chart 4) upon treatment with imines **2a, 2f**, and **2g**, respectively (Table 1).

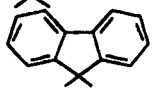
(2-Benzothiazolylchloromethyl)lithium (**1f**), prepared by lithiation of **1e**,[19] reacted cleanly with imines **2a-h** producing aziridines **5a-h** (Chart 5) in good to very good yields. In particular, the reaction of **1f** with imine **2d** took place in a diastereoselective manner giving almost

Chart 5



5a: R = Ph; R^1, R^2 = 

5b: R = Ph; R^1, R^2 = 

5c: R = Ph; R^1, R^2 = 

5d: R = R^2 = Ph; R^1 = H

5e: R = SO_2Ph; R^1 = H, R^2 = Ph

5f: R = Ph; $R^1 = R^2$ = Me

5g: R = R^1 = Ph; R^2 = Me

5h: R = Bz; R^1 = Ph; R^2 = H

exclusively the aziridine **5d** which adopts the *E* configuration. The reaction of **1f** with benzylidenebenzenesulfonamide (**2e**) afforded a mixture of isomeric aziridines **5e** in a 4/1 *E*/*Z* ratio. The configuration could be assigned on the basis of the coupling constants between the two aziridine ring hydrogens ($J_{cis} > J_{trans}$).[18]

The exclusive or preferential formation of aziridines of *E* configuration in the addition reaction of (chloromethyl)lithiums **1b** and **1f** to unsymmetrically substituted imines is rather intriguing in view of the fact that a trans stereoselection has been reported in the Darzens condensation reaction of α-halo esters[14b] with imines and a cis stereoselection in the reaction of α-halo carboxamides.[14c] A possible explanation might be given by considering the structural features of (heteroarylchloromethyl)lithiums **1** and the rate-determining step of the whole process of the aziridine formation. There are spectroscopic evidences, produced by Pagani and coworkers,[20] that in heterocyclic azines and azoles of the kind of **1** a substantial proportion of the negative charge is delocalized on the heterocyclic ring as indicated by the relatively high charge demands (defined as the fraction of the π charge transferred to the heterocyclic moiety from the carbanionic site) of the heterocyclic systems. Such a propensity of the heterocyclic group to delocalize the negative charge is responsible for the double bond fixation of the exocyclic C=C bond in anions **1**. (Chloromethyl)lithiums **1**, therefore, should exist as an equilibrium of the *Z* and *E* isomeric forms **B** and **C** (which resonate with **A**). Considering the experimental conditions of the Darzens reaction of **1** (THF as the solvent and Li as the cation) the **B**/**C** ratio should be substantially shifted toward the stereoisomer **C**.[21] We presume that the reacting carbanionic species **C** may discriminate between the two enantiotopic faces of the imine, leading

(18) Actually, we isolated just one isomer, and its low coupling constant between the aziridinyl hydrogens seems to suggest the *E* configuration, as observed in the case of formylaziridines: Wartski, L. *Bull. Soc. Chim. Fr.* **1975**, 1663. A $J_{cis} > J_{trans}$ ratio has been observed in the case of certain epoxides: Florio, S.; Ingrosso, G.; Ronzini, L.; Epifani, E. *Tetrahedron* **1991**, *47*, 3365.

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(20) Bradamante, S.; Pagani, G. *Pure Appl. Chem.* **1989**, *61*, 709 and references therein.

(21) There are NMR evidences that the *E*/*Z* ratio of the 2-picolyl anion and similar anions is remarkably affected by the nature of the cation, the solvent, and the presence of crown ethers or cryptands: Hogen-Esch, T. E.; Jenkins, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 3666.

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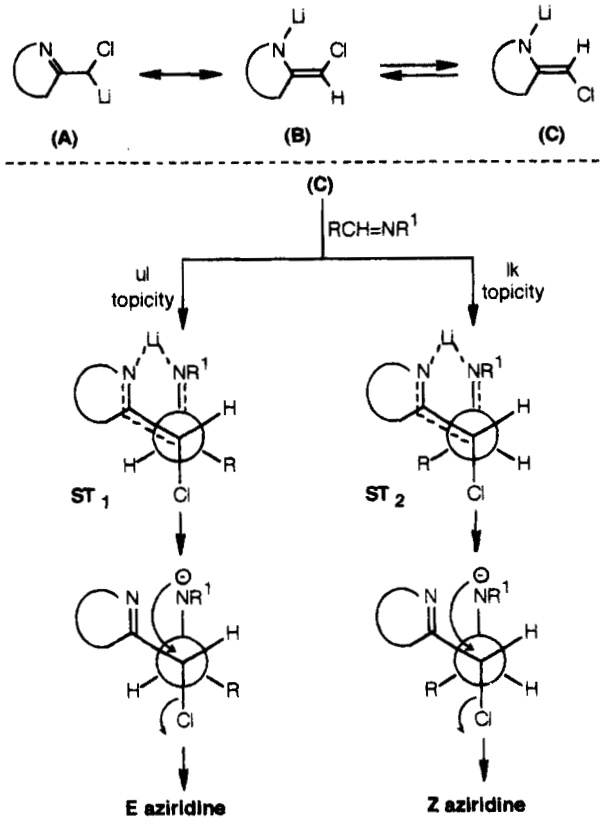
Scheme 2



to transition states $\mathbf{ST_1}$ (*si–re* topicity) and $\mathbf{ST_2}$ (*si–si* topicity). These transition states are both stabilized by the intramolecular chelation of Li, but $\mathbf{ST_1}$, which would evolve to the *E* aziridine, has a lower energy than transition state $\mathbf{ST_2}$ which experiences a higher steric compression and would lead to the *Z* aziridine (Scheme 2). The step, therefore, which keeps under control the stereochemical course of the aziridine fromation, should be that which involves the nucleophilic attack of the (heteroarylchloromethyl)lithium reagent to the imine, as reported for the Darzens condensation reaction of α-halo carboxamides with Schiff bases, though with opposite stereoselection.[14c]

In conclusion, in this paper we have proved that (2-pyridylchloromethyl)- (**1b**), (2-quinolylchloromethyl)- (**1d**), and (2-benzothiazolylchloromethyl)lithium (**1f**), easily available by lithiation of chloromethanes **1a, 1c,** and **1e,** act as Darzens-type reagents and add cleanly and stereoselectively to imines to give heteroarylaziridines. The addition works well with both nonenolizable and enolizable imines. The resulting aziridines have not been described so far and appear to be interesting either as such and as intermediates for the functionalization of pyridine, quinoline, and benzothiazole systems in the side chain. The above Darzens-type reagents are worth being further evaluated for synthetic purposes. To this end, more work is under way in our laboratory.

Experimental Section

^{1}H-NMR spectra were recorded on Varian EM 360A, EM 390, Varian XL-200, and Bruker AM 300 WB spectrometers; chemical shifts are reported in parts per million (δ) from internal standard using $CDCl_3$ as solvent. IR spectra were recorded on a Perkin-Elmer spectrometer Model 598. GC analyses were carried out with a Hewlett-Packard MP-5890 series II gas chromatograph (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.); GC–MS spectrometry analyses were performed on a HP-5890 series II gas chromatograph equipped with HP-5971 mass selective detector operating at 70 eV (E.I.). Melting points were uncorrected. Flash chromatographies were performed with Merck 230–400 mesh silica gel. All reactions were conducted in oven-dried glassware under a nitrogen atmosphere.

Materials. Tetrahydrofuran (THF) of commercial grade was purified by distillation (twice) from sodium wires in N_2 atmosphere. Petroleum ether refers to the 40–60 °C boiling fraction. 2-(Chloromethyl)pyridine (**1a**), and 2-(chloromethyl)quinoline (**1c**) are sold as hydrochlorides (Aldrich) from which they can be obtained upon treatment with 10% NaOH solution. 2-(Chloromethyl)benzothiazole (**1e**) was prepared as reported.[19]

All other chemicals were of commercial grade and used without further purification or eventually distilled prior to use. Microanalyses were performed on a Carlo Erba C,H,N analyzer.

Representative Experimental Procedure. The reaction of 2-(pyridylchloromethyl)lithium (**1b**) with cyclohexylideneaniline (**2a**) is described as an example. To diisopropylamine (2.4 mmol) in 10 mL of THF was added at 0 °C 1 mL of 2.4 M hexane solution of n-BuLi. To the resulting dark yellow solution, cooled at −78 °C, was added dropwise a solution of **1a** (0.256 g, 2.0 mmol) and cyclohexylideneaniline (**2a**) (2.4 mmol) in 10 mL of THF. After 1 h at −78 °C the reaction mixture was allowed to warm to rt and quenched with aqueous NH_4Cl after 6 h. Extraction with ether (3 × 25 mL), drying over Na_2SO_4, and evaporation of the solvent under reduced pressure left a residue that was column chromatographed (silica gel, petroleum ether/ether 7/3 as eluent) to give the following compound.

***N*-Phenyl-3′-(2-pyridyl)cyclohexanespiro-2′-aziridine (3a):** oil, 65% yield; ^{1}H-NMR (60 MHz) δ 0.90–2.10 (m, 10H), 3.42 (s,1H), 6.95–8.00 (m, 8H), 8.70–8.90 (m, 1H); MS *m/e* 264 (M^+, 31), 235 (6), 221 (100), 208 (16), 172 (16), 131 (13), 77 (15). Anal. Calcd for $C_{18}H_{20}N_2$: H, 7.63; C, 81.78; N, 10.60. Found: H, 7.70; C, 81.90; N, 10.35.

All the other aziridines showed the following analytical data:

***N*-Phenyl-3′-(2-pyridyl)cyclopentanespiro-2′-aziridine (3b):** oil, 60% yield; ^{1}H-NMR (60 MHz) δ 1.5–1.95 (m, 8H), 3.57 (s,1H), 6.60–8.00 (m, 8H), 8.65–8.85 (m, 1H); MS *m/e* 250 (M^+, 46), 221 (100), 158 (19), 131 (17), 77 (27); IR ($CHCl_3$) ν 3060, 2960, 1620, 1592, 1488, 1435 cm^{-1}. Anal. Calcd for $C_{17}H_{18}N_2$: H, 7.25; C, 81.56; N, 11.19. Found: H, 7.40; C, 81.76; N,11.10.

***N*-Phenyl-3′-(2-pyridyl)fluorenespiro-2′-aziridine (3c):** oil, 50% yield; ^{1}H-NMR (60 MHz) δ 3.2 (s, 1H), 6.00–8.05 (m, 16H), 8.75–8.95 (m, 1H); MS *m/e* 346 (M^+, 100), 328 (7), 268 (49), 267 (96), 239 (21); IR ($CHCl_3$) ν 3060, 2920, 1600, 1495, 1450, 1435 cm^{-1}. Anal. Calcd for $C_{25}H_{18}N_2$: H, 5.24; C, 86.68; N, 8.09. Found: H, 5.42; C, 86.77; N, 8.00.

***N*-Phenyl-2′-phenyl-3′-(2-pyridyl)aziridine (3d):** oil, 60% yield; ^{1}H-NMR (60 MHz) δ 3.4–3.65 (dd, 2H, *J* = 7 Hz), 6.7–7.4 (m, 13H), 8.15–8.45 (m, 1H); MS *m/e* 272 (M^+, 54), 271 (28), 195 (100), 180 (44), 152 (4), 77 (18). Anal. Calcd for $C_{19}H_{16}N_2$: H, 6.10; C, 86.32; N, 10.60. Found: H, 6.25; C, 86.53; N, 10.50.

***N*-Tosyl-2′-phenyl-3′-(2-pyridyl)aziridine (3e):** oil, 60% yield; ^{1}H-NMR (60 MHz) δ 5.1–5.65 (dd, 2H, *J* = 6.0Hz), 7.3–8.5 (m, 13H), 8.65–8.85 (m, 1H); MS *m/e* 245 (M^+ − 91, 20), 181 (4), 141 (40), 104 (26), 77 (100), 51 (23). Anal. Calcd for $C_{19}H_{16}N_2O_2S$: H, 4.79; C, 67.84; N, 8.33. Found: H, 4.93; C, 67.50; N, 8.30.

***N*-Phenyl-2′-dimethyl-3′-(2-pyridyl)aziridine (3f):** oil, 55% yield; ^{1}H-NMR (60 MHz) δ 1.17 (s, 3H), 1.20 (s, 3H), 3.33 (s, 1H), 6.93–7.90 (m, 8H), 8.63–8.80 (m, 1H); IR (neat) ν 3060, 2930, 1590, 1485, 1380 cm^{-1}. Anal. Calcd for $C_{15}H_{16}N_2$: H, 7.19; C, 80.32; N, 12.49. Found: H, 7.25; C, 80.40; N, 12.50.

***N*-Phenyl-2′-methyl-2′-phenyl-3′-(2-pyridyl)aziridine (3g):** oil, 55% yield; ^{1}H-NMR (60 MHz) δ 1.57 (s, 3H), 3.77 (s, 1H), 6.93–7.97 (m, 13H), 8.50–8.70 (m, 1H); MS *m/e* 286 (M^+, 17), 285 (11), 271 (100), 209 (30), 194 (80), 167 (19), 92 (4), 77 (20). Anal. Calcd for $C_{20}H_{18}N_2$: H, 6.34; C, 83.88; N, 9.78. Found: H, 6.44; C, 83.92; N, 9.73.

***N*-Phenyl-3′-(2-quinolyl)cyclohexanespiro-2′-aziridine (4a):** oil, 60% yield; ^{1}H-NMR (200 MHz) δ 1.1–1.87 (m, 10H), 3.54 (s, 1H), 6.94–8.16 (m, 11H); MS *m/e* 314 (M^+, 82), 299 (26), 271 (48), 208 (47), 172 (35), 159 (54), 143 (100), 128 (16). Anal. Calcd for $C_{22}H_{22}N_2$: H, 7.05; C, 84.04; N, 8.91. Found: H, 7.15; C, 84.19; N, 8.85.

***N*-Phenyl-2′-dimethyl-3′-(2-quinolyl)aziridine (4b):** oil, 40% yield; ^{1}H-NMR (60 MHz) δ 1.23 (s, 3H), 3.63 (s, 1H), 8.47

(m, 11H); MS *m/e* 274 (M^+, 43), 273 (40), 259 (100), 183 (14, 182 (15), 143 (32), 142 (34). Anal. Calcd for $C_{19}H_{18}N_2$: H, 6.61; C, 83.18; N, 10.21. Found: H, 6.70; C, 83.35; N, 10.10.

***N*-Phenyl-2′-methyl-2′-phenyl-3′-(2-quinolyl)aziridine (4c):** oil, 20% yield; ^{1}H-NMR (60 MHz) δ 1.60 (s, 3H), 4.0 (s, 3H), 7.0–8.3 (m, 16H); MS *m/e* 336 (M^+, 76), 335 (93), 321 (100), 259 (26), 244 (49), 230 (25), 194 (33), 142 (79), 115 (21), 103 (27), 77 (51), 51 (12). Anal. Calcd for $C_{24}H_{20}N_2$: H, 5.99; C, 85.68; N, 8.33. Found: H, 5.63; 85.51; N, 8.28.

***N*-Phenyl-3′-(2-benzothiazolyl)cyclohexanespiro-2′-aziridine (5a):** mp 100–102 °C (MeOH/H_2O), 85% yield; ^{1}H-NMR (200 MHz) δ 0.81–1.87 (m, 10H), 3.57 (s, 1H), 6.95–8.01 (m, 9H); MS *m/e* 320 (M^+, 100), 305 (17), 277 (28), 196 (49), 172 (29), 159 (29), 77 (39); IR ($CHCl_3$) ν 3060, 2930, 1595, 1490, 1405, 1270 cm^{-1}. Anal. Calcd for $C_{20}H_{20}N_2S$: H, 6.29; C, 74.96; N, 8.74. Found: H, 6.60; C, 75.23; N, 8.45.

***N*-Phenyl-3′-(2-benzothiazolyl)cyclopentanespiro-2′-aziridine (5b):** mp 92–93 °C (ligroin), 70% yield; ^{1}H-NMR (60 MHz) δ 1.5–2.2 (m, 8H), 3.83 (s, 1H), 6.95–8.40 (m, 9H); MS *m/e* 306 (M^+, 100), 291 (28), 277 (20), 201 (23), 171 (33), 77 (48); IR ($CHCl_3$) ν 3060, 2960, 1600, 1490, 1438, 1390 cm^{-1}. Anal. Calcd for $C_{19}H_{18}N_2S$: H, 5.92; C, 74.47; N, 9.14. Found: H, 5.72; C, 74.65; N, 9.10.

***N*-Phenyl-3′-(2-benzothiazolyl)fluorenespiro-2′-aziridine (5c):** mp 174–5 °C, 75% yield; ^{1}H-NMR (200 MHz) δ 6.72 (s, 1H), 6.79–7.07 (m, 4H), 7.10–7.62 (m, 8H), 7.65–7.99 (m, 4H), 8.10–8.28 (m, 1H); MS *m/e* 402 (M^+, 375), 267 (211), 238 (162), 237 (999). Anal. Calcd for $C_{27}H_{18}N_2S$: H, 4.51; C, 80.57; N, 6.96. Found: H, 4.80; C, 80.34; N, 6.66.

***N*-Phenyl-2′-phenyl-3′-(2-benzothiazolyl)aziridine (5d):** mp 124–125 °C (ligroin), 75% yield. The ^{1}H-NMR spectrum before purification by crystallization clearly indicates the presence of both the cis and trans isomers (trans/cis ~ 4:1): ^{1}H-NMR (90 MHz) (trans) δ 3.3–3.65 (dd, 2H, J = 7.0 Hz); (cis) δ 3.30–3.65 (dd, 2H, J = 7.0 Hz); 7.10–8.30 (m, 14H). Anal. Calc. for $C_{21}H_{16}N_2S$: H, 4.91; C, 76.80; N, 8.53. Found: H, 4.72; C, 76.50; N, 8.47.

***N*-Tosyl-2′-phenyl-3′-(2-benzothiazolyl)aziridine (5e):** mp 42–45 °C (MeOH), 60% yield (cis + trans; trans/cis ~4/1); ^{1}H-NMR (300 MHz) (trans) δ 4.48(d, 1H, J = 4.20 Hz), 4.73 (d, 1H, J = 4.02 Hz), 7.33–8.05 (m, 14H); (cis) δ 4.56–4.58 (dd, 2H, J = 7.16 Hz), 7.13–8.13 (m, 14H); MS *m/e* 250 (M^+ – 142, 100), 249 (460), 146 (24), 120 (13), 103 (18). Anal. Calcd for $C_{21}H_{16}N_2O_2S_2$: H, 4.11; C, 64.26; N, 7.14. Found: H, 4.02; C, 64.01; N, 7.34.

***N*-Phenyl-2′-dimethyl-3′(2-benzothiazolyl)aziridine (5f):** mp 40–42 °C (ligroin), 65% yield; ^{1}H-NMR (60 MHz) δ 1.26 (s, 3H), 1.45 (s, 3H), 3.63 (s, 1H), 6.96–8.30 (m, 9H); MS *m/e* 280 (M^+, 100), 265 (63), 162 (16), 148 (61), 118 (69), 77 (52); IR ($CHCl_3$) ν 3060, 2980, 1600, 1490, 1390, 1380, 1250 cm^{-1}. Anal. Calcd for $C_{17}H_{16}N_2S$: H, 5.75; C, 72.82; N, 9.99. Found: H, 5.53; C, 72.52; N, 9.85.

***N*-Phenyl-2′-methyl-2′-phenyl-3′-(2-benzothiazolyl)-aziridine (5g):** mp 45 °C, 30% yield; ^{1}H-NMR (200 MHz) δ 1.55 (s, 3H), 3.97 (s, 1H), 7.06–7.96 (m, 14H); MS *m/e* 280 (M^+, 100), 327 (18), 250 (36), 207 (29), 180 (81), 148 (64), 103 (26), 77 (60); IR ($CHCl_3$) ν 3060, 2920, 1600, 1490, 1435, 1385 cm^{-1}. Anal. Calcd for $C_{22}H_{18}N_2S$: H, 5.30; C, 77.16; N, 8.18. Found: H, 5.11; C, 77.03; N, 8.28.

***N*-Benzyl-2′-phenyl-3′-(2-benzothiazolyl)aziridine (5h):** mp 89–91 °C; 77% yield; ^{1}H-NMR (trans + cis) (300 MHz) δ 3.37–3.52 (dd, 2H trans, J = 6.5 Hz), 3.42–3.49 (dd, 2H cis, J = 7.0 Hz), 3.61–3.80 (dd, CH_2Ph cis, J = 13.3 Hz), 3.89–3.99 (dd, CH_2Ph trans, J = 13.5 Hz), 7.05–7.90 (m, 14 Ar*H* cis + 14 Ar*H* trans); MS *m/e* 342 (M^+, 156), 281 (67), 239 (734), 207 (238), 194 (999). Anal. Calcd for $C_{22}H_{18}N_2S$: H, 5.52; C, 80.45; N, 8.53. Found: H, 5.30; C, 80.31; N, 8.64.

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