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A FACILE SYNTHESIS OF N-ARYL AZIRIDINES

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ABSTRACT

Reaction of N-aryl-β-amino alcohols with p-toluenesulphonyl chloride under phase transfer catalytic condition gave the corresponding N-aryl aziridines in good yields, whereas N-alkyl-β-amino alcohol [for e.g., L-ephedrine] gave the corresponding N-tosyl derivative as the major product, along with the expected N-alkyl aziridines in lower yield.

The aziridine ring is a versatile building block for organic synthesis, not only because the ring opening of aziridines provides a convenient entry to the stereoselective preparation of functionalized amino compounds, but also because the exocyclic N-substituent modulates the properties and reactivity of the three membered ring.[1–4] The growing importance of functionalized aziridines in organic synthesis and its presence in numerous biomolecules suggest that a general synthetic procedure leading to -C- and -N- substituted aziridines under essentially neutral conditions would be attractive. So far reported classical methods for the synthesis of N-aryl aziridines are: (a) ring closure of N-aryl β-amino alcohol by Gabriel

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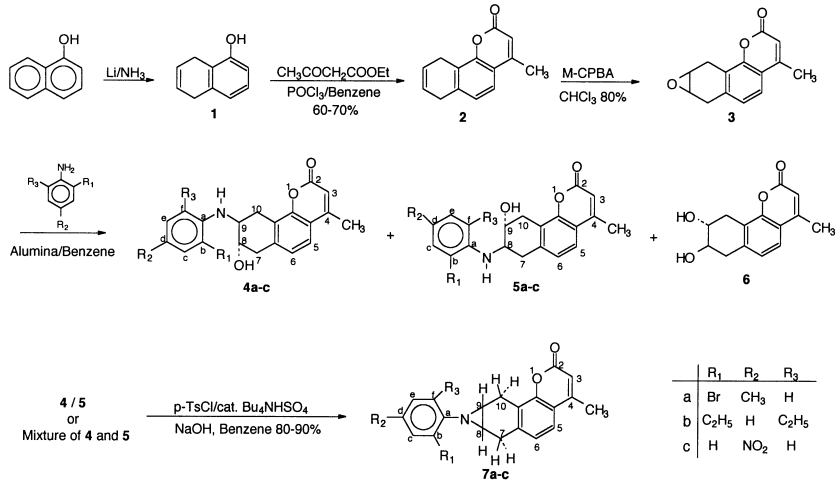
and Wenker synthesis, which suffers from side reactions like dimerization, polymerization, elimination; further, it requires strongly acidic or basic conditions,[5–7] (b) addition of carbenoids to imines or addition of nitrenoids to electron deficient alkenes catalyzed either by Lewis acid or transition metal complexes,[8–11] (c) the cyclodehydration of N-alkyl-β-amino alcohol using triphenylphosphine dihalide, diethoxytriphenylphosphorane wherein triphenylphosphine oxide and 1,4-diphenylpiperazine formed as side products complicate the isolation of the expected products; moreover, application of this method to N-aryl aziridines has received scant attention.[12,13] Although the Lewis-acid catalyzed addition of aryl azides to alkenes gave the expected N-aryl aziridines, it undergoes subsequent ring opening, furnishing either amino alkenes or β-chloro amines as a major product if $AlCl_3$ is used as a Lewis acid.[14]

In continuation of our effort on the synthesis of bioactive heterocyclic compounds,[15–19] we have developed a mild and convenient method of cyclizing N-aryl-β-amino alcohol to N-aryl aziridines under phase transfer catalytic conditions in fairly good yields, which is herein reported.

The Pechmann reaction of 5,8-dihydro-1-naphthol, which was obtained by the Birch reduction of 1-naphthol,[20] with ethyl acetoacetate in the presence of $POCl_3$, furnished the expected 4-methyl-7,10-dihydrobenzo[h]coumarin **2**. Epoxidation of **2** with m-CPBA furnished the anticipated 4-methyl-7,8,9,10-tetrahydro-8,9-epoxybenzo[h]coumarin **3**. Treatment of the epoxide **3** with 2-bromo-4-methylaniline furnished two regioisomeric N-aryl-β-amino alcohols ($\sim$50:50) viz., 9-(2-bromo-4-methylanilino)-8-hydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzo[h]coumarin **4a**, 8-(2-bromo-4-methylanilino)-9-hydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzo[h]coumarin **5a** in an overall yield of $>80\%$ along with 8,9-dihydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzo[h]coumarin **6** ($<10\%$) as a minor product. The two regioisomers and the diol were separated by column chromatography. The structures of the two regioisomers and the diol were assigned by spectral, analytical data and further the structure of the regioisomer **5a** has been confirmed by XRD.[21]

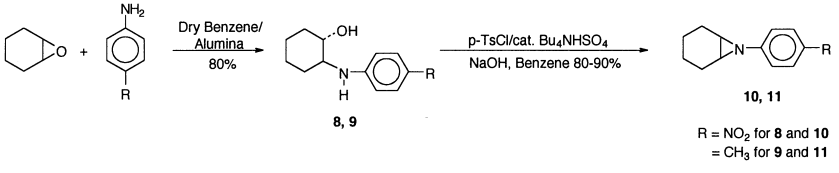
Treatment of **4a** with 1.2 equiv. of p-toluenesulphonyl chloride, 50% NaOH, and 0.2 equiv. of n-Bu_4NHSO_4 in benzene furnished the expected aziridine **7a** in less than half an hour. Similarly, the reaction with regioisomeric alcohol **5a** under the same condition furnished the same aziridine **7a**. Hence, the later experiments were carried out with a mixture of regioisomeric alcohols. A blank reaction was also carried out in the absence of PTC, which resulted only in the recovery of the starting material. Extension of the reaction to the mixture of N-aryl-β-amino alcohols **4b** and **5b**, as well as **4c** and **5c**, under the aforesaid condition furnished the expected N-aryl aziridines **7b** and **7c**, respectively, in good



Scheme 1.

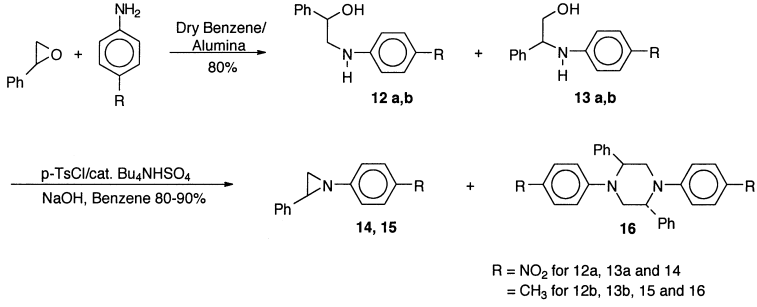
yields (Scheme 1). The new N-arylaziridines **7a–c** were characterized well by spectral, analytical data and further the aziridine **7a** has been confirmed by x-ray studies.[22]

Since a systematic literature survey revealed that this method is new and facile, we extended this method to the synthesis of several known and new N-aryl aziridines for generalisation. Cyclohexene oxide was opened with p-nitroaniline and p-toluidine to afford the respective ring-opened compounds **8** and **9**. Then the treatment of **8** and **9** under our experimental condition furnished the expected N-arylaziridines **10** and **11** in good yields. The cyclodehydration of **4a**, **5a**, **8**, and **9** using triphenylphosphine dihalide/Et_3N or triphenylphosphine-diethyl azodicarboxylate (Mitsunobu reagent) did not give the expected aziridines; to our surprise, only the starting materials were recovered. The structures of **10** and **11** have been determined by the spectral, analytical data and further the structure of **10** has been confirmed by XRD[23] (Scheme 2).



Scheme 2.

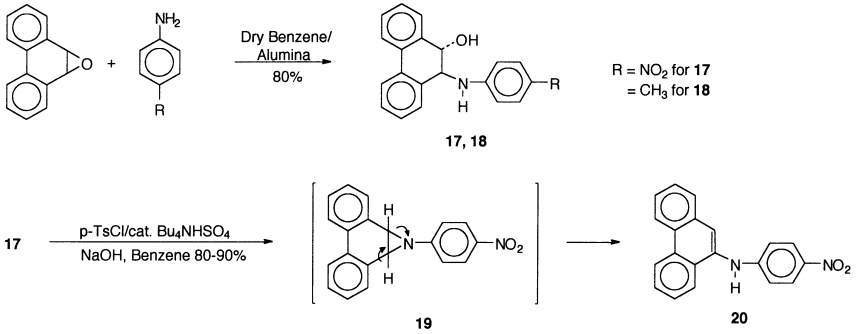
Next, styrene oxide was opened with p-nitroaniline to afford 2-hydroxy-N-(4-nitrophenyl) phenethylamine **12a** as the major product and 2-(4-nitroanilino)-phenethylalcohol **13a** as the minor product. The structures of these two regioisomers were duly characterized by spectral and analytical data and further evidenced by XRD.[24,25] Treatment of either **12a** or **13a** under our reaction condition gave the expected aziridine **14**. The structure of **14** is in accordance with literature data.[26] Similarly, the regioisomeric mixture of N-p-tolyl-β-amino alcohols **12b** and **13b**, which were obtained from the reaction of styrene oxide and p-toluidine under our experimental condition, gave the expected N-aryl aziridine **15** (80%) along with trans-1,4-di(4-methylphenyl)-2,5-diphenyl-piperazine **16** (15%). The structures of **15**[27] and **16** were confirmed by spectral and analytical data (Scheme 3).



Scheme 3.

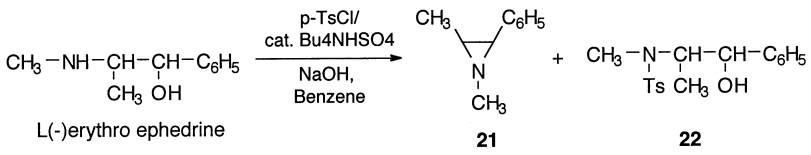
Next we were very much interested to synthesize polycyclic imines by our method because of their biological relevance and the reports of unsuccessful attempts in the literature.[28] Phenanthrene-9,10-oxide was opened by p-nitroaniline and p-toluidine to give the ring-opened compounds **17** and **18**, respectively. Treatment of **17** under the aforesaid condition furnished N(-4-nitrophenyl)-9-aminophenanthrene **20** in 30% yield instead of the expected N-aryl aziridine **19**. During the course of the reaction, TLC analysis showed the complete disappearance of the starting materials with the appearance of a new spot. However, during work-up the new spot completely disappeared with the appearance of another spot on TLC. It was separated and identified as **20**. It has been reported that polycyclic imino compounds, which have electron-withdrawing groups attached to the nitrogen atom, rearranged readily at ambient temperature to aromatic amines. For example, the rearrangement of 1-acetyl-1a, 9c-dihydrophenanthr[9,10-b]azirine to N-acetyl-9-amino phenanthrene is well known.[29] Hence, the isolation of the compound **20** indirectly confirms the

formation of N-(4-nitrophenyl)-phenanthr[9,10-b]aziridine **19** (which would have readily rearranged to **20** as a stable product). Treatment of **18** under our reaction condition gave no characterizable product (Scheme 4). So far, we have witnessed that the reaction of N-aryl-β-aminoalcohols with p-TsCl under phase transfer condition gave the corresponding N-aryl aziridines in good yields.



Scheme 4.

As a further application of our method to synthesize N-alkyl aziridines, we took L-ephedrine as the starting material. The reaction of L-ephedrine furnished two products under the aforesaid condition and were identified as the expected (+) trans-1,2-dimethyl-3-phenylaziridine **21** (20%) and the corresponding N-tosylated product **22** (78%). Our effort to improve the yield of aziridine by changing the condition such as base concentration, catalyst variation, and solvent variation ($CHCl_3$, CH_2Cl_2, and toluene), gave no fruitful results (Scheme 5).



Scheme 5.

In conclusion, this method provides a mild and convenient way of cyclizing (N-aryl-β-aminoalcohol to the corresponding N-aryl aziridines and has some advantages over the known classical method because of the mild reaction condition, simplicity of performance, and good yields, which make this method a useful addition to the existing methodology.

EXPERIMENTAL

Melting points were determined by using a Toshniwal melting point apparatus in an open capillary tube and are uncorrected. IR spectra were recorded in Nicolet Impact 400 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded on Jeol 400 MHz, Brucker 300 MHz, Bruker ARX 200 MHz, and Jeol FX 90Q spectrometers, using TMS as internal standard. GC/MS data were obtained from a Jeol-DX-303 spectrometer. Microanalyses were performed in a Perkin-Elmer 240B element analyzer. Chromatography was performed on silica gel (ACME, 100–200 mesh), and purified according to the reported procedure.[30] Phenanthrene oxide was prepared by the literature method.[31]

4-Methyl-7,10-dihydrobenzo[h]coumarin (2)

A mixture of 5,8-dihydro-1-naphthol[7] (1.46 g, 0.01 mol), ethyl acetoacetate (1.56 g, 0.012 mol), and phosphoryl chloride (1.53 g, 0.01 mol) was refluxed in dry benzene (30 mL) for 12 h. Then solvent was removed under vacuum and to the residue was added 30 mL of ice-water and 50 mL of CH_2Cl_2, neutralized with saturated aqueous $NaHCO_3$ to pH = 7, and extracted with CH_2Cl_2 (3×50 mL). The combined extracts were washed with water, brine, and dried ($MgSO_4$). After removal of the solvent under vacuum, the residue was chromatographed over silica gel using a mixture of hexane-EtOAc (9:1) as eluant to afford **2**, (1.48 g, 70%).

M.p. 150°–152°C. IR (KBr): $\nu = 2900, 2800, 2760, 1720, 1600\ cm^{-1}$. ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 2.3$ (s, 3H, CH_3), 3.4 (bs, 4H, $2CH_2$), 5.8–5.9 (m, 2H, 2CH), 6.2 (s, 1H, H_3), 6.90 (d, 1H, J = 9 Hz, Ar-H_5), 7.3 (d, 1H, J = 9 Hz, Ar-H_6). MS (EI) m/z (%) = 212 (100), 204 (48), 184 (36), 183 (28), 169 (34), 167 (86), 165 (62), 155 (20), 144 (22), 143 (38), 142 (24), 132 (42), 130 (60), 119 (24), 98 (16), 97 (22), 95 (52). Anal. calc. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.00; H, 5.59. Further, the structure of **2** has been confirmed by XRD.[32]

4-Methyl-7,8,9,10-tetrahydro-8,9-epoxybenzo[h]coumarin (3)

A mixture of the compound **2** (2.12 g, 0.01 mol) and m-CPBA (1.725 g, 0.01 mol) in anhydrous chloroform (50 mL) was stirred overnight at room temperature. After the disappearance of the starting material on TLC, dil. aqueous $NaHCO_3$ was added to the reaction mixture while stirring at 0°C. The organic layer was separated, washed several times with water, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the

concentrate on crystallization from $CHCl_3$ furnished **3** as colorless needless (1.93 g, 85%).

M.p. 198°–200°C. IR (KBr): $\nu = 3100$, 3000, 2900, 2850, 1710, 1600, 1400, 1190, 1000 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): $\delta = 2.4$ (s, 3H, CH_3), 2.8–3.8 (m, 6H, $2CH_2$ and 2CH), 6.2 (s, 1H, H_3), 6.90 (d, 1H, J = 9 Hz, Ar-H_5), 7.40 (d, 1H, J = 9 Hz, Ar-H_6). MS (EI): m/z (%) = 228 (100), 213 (10), 199 (40), 185 (5), 171 (20), 128 (38), 115 (30), 102 (5), 91 (5), 77 (5). HRMS (positive FAB): $m/z = M^+$ calculated for $C_{14}H_{12}O_3$: 228.078644. Found: 228.079200. Further, the structure of the compound **3** has been confirmed by XRD.[32]

General Procedure for Ring Opening of the Epoxide

A mixture of the activated alumina (7.5 g per 1 g epoxide), aniline (1.3 equiv.), and epoxide in anhydrous benzene (50 mL) was refluxed under nitrogen atmosphere, until the TLC analysis showed the complete disappearance of the epoxide. The reaction mixture was cooled and filtered through a sintered funnel under vacuum; the alumina was repeatedly washed with dry methanol. Removal of the solvent under vacuum gave a viscous oil, which was purified by column chromatography using silica gel and eluted with hexane-ethyl acetate (8:2) to get the respective ring-opened compound.

9-(2-Bromo-4-methylanilino)-8-hydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin (**4a**), 8-(2-bromo-4-methylanilino)-9-hydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin (**5a**), and 8,9-dihydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin (**6**)

Compound **4a**, **5a**, and **6** were obtained from the reaction of 4-methyl-7, 8, 9, 10-tetrahydro-8, 9-epoxybenzo[h]coumarin **4** (1.14 g, 5 mmol), 2-bromo-4-methylaniline and activated alumina (7.5 g) using the above general procedure. The reason for the formation of dihydroxy compound **6** may be due to the traces of moisture present in the reaction medium and it could be avoided if the alumina is dried at 120°C in a vacuum oven.

Compound **4a**

Yield: 0.93 g (45%), m.p. 128°–130°C IR (KBr): $\nu = 3450$, 3350, 2900, 1720, 1600, 1510 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.19$ (s, 3H, $ArCH_3$), 2.37 (d, 3H, J = 0.93 Hz, $4CH_3$), 2.65 (dd, 1H, J = 8.5, 7.0 Hz, $10CH_2$), 3.00

(dd, 1H, J = 8.8, 17.20 Hz, $7CH_2$), 3.3 (dd, 1H, J = 5.25, 17.30 Hz, $7CH_2$), 3.6 (dd, 1H, J = 5.3, 17.20 Hz, $10CH_2$), 3.7–3.75 (m, 1H, 9CH), 3.9–4.12 (m, 1H, 8CH), 6.20 (d, 1H, J = 1.03 Hz, 3-H), 6.77 (d, 1H, J = 8.3 Hz, Ar-H_f), 6.92 (dd, 1H, J = 1.4, 8.3 Hz, ArH_e), 7.04 (d, 1H, J = 8.2 Hz, Ar-5H), 7.21 (d, 1H, J = 1.4 Hz, Ar-H_c), 7.37 (d, 1H, J = 8.2 Hz, Ar-6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.59, 19.89, 28.74, 36.46, 55.43, 69.34, 110.83, 113.04, 113.80, 117.53, 122.37, 122.37, 124.63, 128.17, 128.52, 129.00, 132.77, 138.72, 141.85, 151.03, 152.66, 160.70. Anal. calc. for $C_{21}H_{20}NO_3Br$: C, 60.88; H, 4.87; N, 3.38. Found: C, 61.02; H, 4.88; N, 3.40.

Compound **5a**

Yield: 0.820 g (40%), m.p. 196°–198°C. IR (KBr): ν = 3470, 3350, 3000, 2950, 2900, 1720, 1600, 1520, 1450, 1400, 1300, 1190, 1100, 1090, 1040, 880, 800, 770, 690, 590 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3H, Ar-CH_3), 2.43 (d, 3H, J = 1.1 Hz, 4-CH_3), 2.70 (d, 1H, J = 1.65 Hz, OH), 2.81 (dd, 1H, J = 9.15, 7.2 Hz, 7-CH_2), 2.95 (dd, 1H, J = 8.42, 17.90 Hz, 10-CH_2), 3.40 (dd, 1H, J = 5.12, 17.2 Hz, 7-CH_2), 3.6 (dd, 1H, J = 5.67, 17.76 Hz, 10-CH_2), 3.71–3.77 (m, 1H, 8-CH), 4.03–4.16 (m, 1H, 9-CH), 6.26 (d, 1H, J = 0.78 Hz, 3-H), 6.81 (d, 1H, J = 8.42 Hz, Ar-H_f), 6.99–7.11 (m, 2H, Ar-H_e&Ar-5H), 7.24–7.26 (m, 1H, Ar-H_e), 7.40 (d, 1H, J = 8.24 Hz, Ar-6H). ^{13}C NMR (50 MHz, $CDCl_3$): 18.70, 20.01, 30.15, 34.72, 55.28, 69.23, 110.98, 113.27, 114.10, 117.82, 122.11, 122.45, 124.47, 128.72, 129.12, 132.89, 138.64, 141.91, 151.42, 152.63, 160.79. Anal. calc. for $C_{21}H_{20}NO_3Br$: C, 60.88; H, 4.87; N, 3.38. Found: C, 60.80; H, 4.79; N, 3.35.

Compound (**6**)

Yield: 0.062 g (5%), m.p. 190°–192°C. IR (KBr): ν = 3330, 3225, 1721, 1610, 1500, 1470, 1100, 980, 920 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ = 2.41 (d, 3H, J = 1.0 Hz, CH_3), 2.58–2.60 (m, 1H, CH), 2.78–2.91 (m, 1H, CH), 3.40–3.48 (m, 4H, $2CH_2$), 3.80–3.92 (m, 1H, OH). MS (EI): *m/z* (%); 246 (100), 228 (85), 210 (30), 199 (82), 187 (35), 171 (18), 158 (40), 145 (22), 128 (45), 105 (18), 91 (25), 77 (30). Anal. calc. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.35; H, 5.79.

9-(2,6-Diethylanilino)-8-hydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin (**4b**) and 8-(2,6-diethylanilino)-9-hydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin (**5b**)

Following the general procedure, treatment of epoxide **3** (1.14 g, 5 mmol) with 2,6-diethylaniline (0.968 g, 6.5 mmol) gave 1.602 g (85%) of an inseparable mixture of **4b** and **5b**.

8-Hydroxy-4-methyl-9-(4-nitroanilino)-7,8,9,10-tetrahydro-7,8-benzocoumarin (**4c**) and 8-(4-nitroanilino)-9-hydroxy-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin (**5c**)

Following the general procedure epoxide **3** (1.14 g, 5 mmol) and 4-nitroaniline (0.897 g, 6.5 mmol), gave 1.885 g (85%) of an inseparable mixture of **4c** and **5c**.

trans-2-(4-Nitroanilino)cyclohexanol (**8**)

Following the general procedure, use of cyclohexene oxide (0.45 g, 5 mmol) and 4-Nitroaniline (0.897 g, 6.5 mmol), gave 1.12 g (95%) of **8** as yellow-colored crystalline compound.

M.p. 118°–120°C. IR (KBr): $\nu = 3400$, 2975, 2870, 1500, 1600, 1420, 1350, 1340, 1320, 1400 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.30$–1.39 (m, 4H, -CH_2), 1.70–2.18 (m, 4H, CH_2), 3.2–3.4 (m, 2H, 2CH), 4.80 (bs, 2H, NH&OH, D_2O-exchangeable), 6.65 (d, 2H, J = 9.3 Hz, ArH), 7.98 (d, 2H, J = 9.3 Hz). ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 25.30$, 25.0, 32.0, 35.10, 59.01, 75.0, 112.50, 127.29, 137.05, 156.16.

trans-2-(4-Methylanilino)cyclohexanol (**9**)

Following the general procedure, reaction of cyclohexene oxide (0.45 g, 5 mmol) and p-toluidine (0.700 g, 6.5 mmol) gave 0.943 g (92%) of **9** as a viscous liquid.

IR (KBr): $\nu = 3400$, 3000, 1510, 1500, 1200, 890 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.25$–1.40 (m, 4H, $2CH_2$), 1.75–2.09 (m, 4H, $2CH_2$), 2.12 (s, 3H, CH_3), 3.0–3.35 (m, 2H, 2CH), 4.75 (bs, 2H, NH&OH), 6.60 (d, 2H, J = 9.3 Hz, ArH), 7.38 (d, 2H, J = 9.3 Hz, Ar-H). ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 20.5$, 25.3, 32.0, 35.20, 59.05, 69.0, 115.50, 127.0, 135.5, 145.

β-Hydroxy-N(4-nitrophenyl)phenethylamine (**12a**) and 2-(4-nitroanilino)-2-phenylethanol (**13a**)

Following the general procedure, treatment of styrene oxide (0.6 g, 5 mmol) with 4-Nitroaniline (0.897 g, 6.5 mmol), gave 1.03 g (80%) of **12a** and 0.125 g (10%) of **13a**.

Compound **12a**

M.p. 138°–140°C. IR (KBr): $\nu = 3400$, 2950, 1500, 1460, 1340, 1320, 1150, 1200 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.69$–3.75 (m, 1H, CH_2), 3.88–3.93 (m, 1H, CH_2), 4.10 (t, 1H, OH, D_2O-exchangeable), 4.50–4.54 (m, 1H, CH), 6.14 (bs, 1H, NH, D_2O-exchangeable), 6.46 (d, 2H, J=9.28 Hz, Ar-H), 7.30–7.35 (m, 5H, Ar-H, 7.95 (d, 2H, J = 9.28 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 59.98$ (d), 66.67 (t), 112.06 (d), 126.12 (d), 126.58 (d), 127.76 (d), 128.86 (d), 137.72 (s), 139.15 (s), 153.31 (s). Anal. calc. for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 65.0; H, 5.37; N, 10.20.

Compound **13a**

M.p. 96°–98°C. IR (KBr): $\nu = 3410$, 2960, 1500, 1450, 1350, 1310, 1290, 1255, 1175 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.30$–3.45 (m, 2H, CH_2), 4.25 (bs, 1H, NH, D_2O-exchangeable), 4.86–4.90 (m, 1H, CH), 5.46 (t, 1H, OH, D_2O-exchangeable), 6.50 (d, 2H, J = 9.32 Hz, Ar-H), 7.27–7.40 (m, 5H, Ar-H), 7.99 (d, 2H, J = 9.28 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 50.69$ (t), 71.99 (d), 111.20 (d), 125.93 (d), 126.38 (d), 128.05 (d), 128.59 (d), 137.57 (s), 141.89 (s), 153.61 (s). Anal. calc. for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 65.50; H, 5.52; N, 10.98.

2-Hydroxy-N (4-methylphenyl)phenethylamine (**12b**) and
2-(4-Methylanilino)-2-phenylethanol (**13b**)

Following the general procedure, use of styrene oxide (0.6 g, 5 mmol) and p-toluidine (0.7 g, 6.5 mmol) gave 0.930 g (82%) of an inseparable mixture of **12b** and **13b** as a viscous liquid.

trans-10-(4-nitroanilino)-9,10-dihydrophenanthren-9-ol (**17**)

Following the general procedure reaction of 9,10-phenanthrene oxide (0.97 g, 5 mmol) and 4-nitroaniline (0.897 g, 6.5 mmol) gave 1.162 g (70%) of **17** as a yellow crystalline solid.

M.p. 108°–110°C. IR (KBr): $\nu = 3400$, 3300, 3050, 3020, 1600, 1490, 1300, 1120 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): $\delta = 3.75$ (bs, 1H, OH), 4.74 (d, 1H, Ar-CH), 6.53 (d, 1H, Ar-CH), 7.27–7.60 (m, 8H, ArH), 7.71–7.93 (m, 4H, ArH).

trans-2-(4-Methylphenylamino)-9,10-dihydrophenanthren-1-ol (**18**)

Following the general procedure, reaction of 9,10-phenanthrene oxide (0.97 g, 5 mmol) and p-toluidine (0.7 g, 6.5 mmol) gave 1.05 g (70%) of **18** as a brown-colored crystalline solid.

M.p. 154°–156°C. IR (KBr): $\nu = 3420$, 3200, 3000, 1590, 1520, 1420, 1200, 1150 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): $\delta = 2.14$ (s, 3H, Ar-CH_3), 3.05 (bs, 1H, NH), 5.14 (d, 1H, J = 3.8 Hz, Ar-CH), 5.79 (d, 1H, J = 3.56 Hz, Ar-CH), 7.20–7.50 (m, 8H, Ar-H), 7.6–7.8 (m, 4H, Ar-H).

General Procedure for Cyclizing N-aryl-β-Aminoalcohol to N-Aryl Aziridines Under PTC Condition

To a mixture of N-aryl-β-aminoalcohol (0.05 m), p-toluenesulfonyl chloride (0.06 m) and 0.2 equiv. of tetrabutylammonium hydrogensulphate in 50 mL of benzene, was added 5 mL of 50% NaOH. Then the reaction mixture was stirred at room temperature for half an hour. After completion of the reaction, the organic layer was separated and the aqueous layer was extracted twice with ethyl acetate (2×25 mL). The organic layers were combined and washed several times with water, brine, and dried ($MgSO_4$). After removal of the solvent under vacuum, the N-aryl aziridines were obtained either by crystallization or by chromatographic purification using purified silica gel. It was found that the use of commercially available silica gel (which is slightly acidic) gives lower yield of N-aryl aziridines along with respective ring-opened compound. But the use of purified silica gel furnished the N-aryl aziridines in fairly good yields and without any trace of ring-opened compound.

N-(2-bromo-4-methylphenyl)-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin-8,9-aziridine (**7a**)

Following the general procedure using **4a/5a** or a mixture of **4a** and **5a** (0.5 g, 1.20 mmol) and p-toluenesulphonyl chloride (0.276 g, 1.45 mmol) gave 0.391 g (82%) of **7a** as a colorless solid.

M.p. 208°–210°C. IR (KBr): $\nu = 2890$, 1720, 1600, 1490, 1380, 1370, 1210, 1090, 830, 800 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.22$ (s, 3H, Ar-CH_3), 2.37 (d, 3H, J = 1 Hz, 4-CH_3), 2.70 (ddd, 1H, J = 6.59, 3.23, 1.46 Hz, 9-CH), 2.80 (ddd, 1H, J = 6.58, 3.29, 1.64 Hz, 8-CH), 3.05 (dd, 1H, J = 2.74, 18.0 Hz, 10-CH_2), 3.26 (dd, 1H, J = 2.53, 17.6 Hz, 7-CH_2), 3.70 (d, 1H, J = 17.6 Hz, 7-CH_2), 4.10 (d, 1H, J = 18.0 Hz, 10-CH_2),

6.20 (d, 1H, J = 1.0 Hz, 3-CH), 6.85 (d, 1H, J = 8.2 Hz, Ar-H_f), 6.97 (dd, 1H, J = 1.4, 8.2 Hz, Ar-H_e), 7.05 (d, 1H, J = 8.2 Hz, Ar-5H), 7.26 (d, 1H, J = 4.8 Hz, Ar-H_c), 7.37 (d, 1H, J = 8.3 Hz, Ar-6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.65 (q), 20.21 (q), 22.69 (splitt. t, 10-CH_2), 29.88 (t, 7-CH_2), 38.91 (d, 8-CH), 39.54 (d, 9-CH), 113.73 (d), 116.26 (s), 117.93 (s), 121.40 (s), 121.44 (d), 121.97 (d), 125.11 (d), 128.45 (d), 133.17 (s), 133.31 (d), 137.83 (s), 148.70 (s), 151.50 (s), 152.77 (s), 160.97 (s). MS (EI): *m/z* (%) = 395 (100), 379 (65), 361 (35), 348 (10), 316 (20), 297 (30), 288 (15), 255 (10), 219 (30), 210 (45), 198 (60), 182 (30), 152 (25), 127 (35), 110 (30), 95 (25), 85 (25), 73 (42), 67 (30). Anal. calc. for $C_{21}H_{18}NO_2Br$: C, 63.65; H, 4.58; N, 3.53. Found: C, 63.67; H, 4.48, N, 3.14.

N-(2,6-diethylphenyl)-4-methyl-7,8,9,10-tetrahydro-7,8-benzo-coumarin-8,9-aziridine (**7b**)

Following the general procedure, reaction of a mixture of regioisomers of **4b** and **5b** (0.5 g, 1.32 mmol) and p-toluenesulphonyl chloride (0.303 g, 1.59 mmol) gave 0.415 g (90%) of **7b** as a colorless solid.

M.p. 158°–160°C. IR (KBr): ν = 2970, 2910, 2870, 1720, 1600, 1450, 1400, 900 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, 6H, 2CH_3), 2.40 (d, 3H, J = 0.96 Hz, 4-CH_3), 2.67–2.80 (m, 6H, 8-CH, 9-CH&2Ar-CH_2), 3.02 (dd, 1H, J = 18.08 Hz, 10CH_2), 3.28 (dd, 1H, J = 15.6 Hz, 7-CH_2), 3.59 (d, 1H, J = 17.6 Hz, 7-CH_2), 4.07 (d, 1H, J = 18.08, 10-CH_2), 6.23 (d, 1H, J = 1 Hz, 3-CH), 6.84–6.88 (m, 1H, Ar-H_c), 6.98 (d, 2H, J = 7.8 Hz, Ar-H_b&H_d), 7.08 (d, 1H, J = 8.32 Hz, Ar-H_5), 7.39 (d, 1H, J = 8.28 Hz, Ar-H_6). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.05 (q), 18.70 (q), 22.61 (splitt. t), 25.03 (t), 29.96 (t), 38.96 (d), 113.89 (d), 118.09 (s), 121.64 (s), 121.95 (d), 120.05 (d), 125.0 (d), 126.53 (d), 135.01 (d), 138.04 (s), 138.03 (s), 150.03 (s), 151.56 (s), 152.73 (s), 160.99 (s). MS (EI): *m/z* (%) = 359 (100), 358 (85), 343 (25), 316 (65), 256 (40), 199 (60), 182 (45), 171 (55), 153 (50), 101 (15), 56 (70). Anal. calc. for $C_{24}H_{25}NO_2$: C, 80.19; H, 7.01; N, 3.90. Found: C, 80.50; H, 6.95; N, 3.70.

N-(4-nitrophenyl)-4-methyl-7,8,9,10-tetrahydro-7,8-benzocoumarin-8,9-aziridine (**7c**)

Following the general procedure, use of a mixture of regioisomers **4c** and **5c** (0.5 g, 1.36 mmol) and p-toluenesulphonyl chloride (0.312 g, 1.64 mmol) gave 0.420 g (85%) of **7c** as a colorless compound.

M.p. 210°–212°C. IR (KBr): $\nu = 3100$, 2950, 2970, 1720, 1600, 1500, 1350 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.40$ (d, 3H, J = 1.16 Hz, 4-CH_3), 2.86–2.95 (m, 2H, 8-CH&9-CH), 3.05 (d, 1H, J = 18.64 Hz, 10-CH_2), 3.29 (d, 1H, J = 17.7 Hz, 7-CH_2), 3.55 (d, 1H, J = 17.5 Hz, 7-CH_2), 3.99 (d, 1H, J = 18.10 Hz, 10-CH_2), 6.24 (d, 1H, J = 1.08 Hz, 3-CH), 7.04–7.10 (m, 3H, Ar-H), 7.35–7.44 (m, 1H, Ar-H), 8.08–8.13 (m, 2H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$); $\delta = 18.67$, 22.88, 30.11, 38.72, 38.99, 114.09, 118.22, 120.52, 120.97, 122.34, 125.07, 128.29, 137.17, 142.56, 151.48, 152.64, 160.68, 160.60. Anal. calc. for $C_{20}H_{16}N_2O_4$: C, 68.97; H, 4.63; N, 8.04. Found: C, 69.50; H, 4.49; N, 7.95.

7-(4-Nitrophenyl)-7-azabicyclo[4.1.0]-heptane (**10**)

Following the general procedure, reaction of **8** (0.5 g, 2.12 mmol) with p-toluenesulphonyl chloride (0.485 g, 2.54 mmol) gave 0.450 g (99%) of **10** as a yellow crystalline compound.

M.p. 90°–92°C. IR (KBr): $\nu = 3100$, 3050, 3000, 2970, 2870, 1590, 1500, 1400, 1340, 1280, 1100, 1090 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.23$–1.46 (m, 4H, $2CH_2$), 1.49–1.59 (m, 4H, $2CH_2$), 1.88–2.33 (m, 2H, 2-CH), 7.00 (d, 2H, J = 9.02 Hz, Ar-H), 8.08 (d, 2H, J = 9.04 Hz, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$); $\delta = 20.07$, 24.29, 39.42, 120.22, 125.03, 142.11, 162.06, Anal. calc. for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.47; N, 12.84. Found: C, 65.70; H, 6.60; N, 12.70.

7-(4-Methylphenyl)-7-azabicyclo[4.1.0]-heptane (**11**)

Following the general procedure, reaction of **9** (0.5 g, 2.43 mmol) with p-toluene sulphonylchloride (0.558 g, 2.93 mmol) gave 0.350 g (75%) of **11** as a viscous liquid.

IR (KBr): $\nu = 3000$, 2950, 2950, 1520, 1500, 1420 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.20$–1.40 (m, 4H, $2CH_2$), 1.35–1.45 (m, 4H, $2CH_2$), 1.80–2.20 (m, 2H, 2CH), 2.30 (s, 3H, CH_3), 6.65 (d, 2H, J = 9.2 Hz, Ar-H), 7.25 (d, 2H, J = 9.2 Hz, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$); $\delta = 20.60$, 20.05, 24.0, 39.0, 120.18, 125.60, 140.50, 152.8. Anal. calc. for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.28; H, 9.10; N, 7.39.

N-(4-nitrophenyl)-2-phenyl-aziridine (**14**)

Following the general procedure using **12a**/**13a** or a mixture of **12a** and **13a** (0.5 g, 1.93 mmol) and p-toluenesulphonyl chloride (0.443 g, 2.32 mmol), **14** was obtained 0.372 g (80%), as a yellow solid.

M.p. 132°–134°C. Lit: 135°C.[26] IR (KBr): $\nu = 3100$, 3080, 2950, 1620, 1530, 1450, 1320, 1280 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ=3.68 (dd, J = 14.0, 9.8 Hz, CH_2), 4.01 (dd, 1H, J = 14.6, 4.9 Hz, CH_2), 4.85 (dd, 1H, J = 9.8, 4.9 Hz, benzylic-H), 7.00 (d, 2H, J = 9.0 Hz, Ar-H), 7.30–7.52 (m, 5H, Ar-H), 8.05 (d, 2H, J=9.0 Hz, Ar-H).

N-(4-methylphenyl)-2-phenyl-aziridine (**15**) and trans-1,4-di(4-methylphenyl)-2,5-diphenylpiperazine (**16**)

Treatment of a mixture **12b** and **13b** (0.5 g, 2.20 mmol) with p-toluenesulphonyl chloride (0.50 g, 2.64 mmol) gave 0.322 g (70%) of **15** as a colorless solid and 0.135 g (15%) of **16**.

Compound 15

M.p. 162°–164°C. IR (KBr): $\nu = 3000$, 3070, 2970, 2900, 1620, 1520, 1450, 1370, 810, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.17$ (s, 3H, Ar-CH_3), 3.70 (dd, J = 14.2, 9.80 Hz, CH_2), 4.05 (dd, 1H, J = 14.64, 4.88 Hz, CH_2), 4.80 (dd, 1H, J = 9.8, 4.88, benzylic-H), 6.67 (d, 2H, J = 8.32 Hz, Ar-H), 6.93 (d, 2H, J = 8.32 Hz, Ar-H), 7.20–7.40 (m, 5H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.23$ (q), 50.86 (t), 61.05 (d), 114.55 (d), 126.42 (d), 127.19 (s, d), 128.70 (d), 129.63 (d), 141.42 (s), 146.73 (s), MS (EI): m/z (%) = 209 (25), 208 (100), 194 (85), 193 (90), 118 (85), 91 (45). Anal. calc. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.90; H, 7.30; N, 7.02.

Compound 16

M.p. 256°–258°C. IR (KBr): $\nu = 3040$, 2950, 2900, 2840, 2800, 1600, 1510, 1220, 1120, 920, 810, 740, 680 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.16$ (s, 6H, 2Ar-CH_3), 3.30 (dd, 2H, J = 9.28, 12.68 Hz, 2-CH_2), 3.77 (dd, 2H, J = 3.4, 12.68 Hz, 2-CH_2), 4.59 (dd, 2H, J = 3.4, 9.28 Hz, 2-Benzylic-H), 6.74 (d, 4H, J = 8.32 Hz, 4-Ar-H), 6.86 (d, 4H, J = 8.32 Hz, 4-Ar-H), 7.10–7.37 (m, 10H, Ar-H). MS (EI): m/z (%) = 418 (65), 298 (40),

222 (50), 208 (7), 195 (90), 119 (100), 104 (80), 103 (50), 91 (45). Anal. calc. for $C_{30}H_{30}N_2$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.00; H, 7.20; N, 6.65.

9-Amino-N-(4-Nitrophenyl)phenanthrene (**20**)

Reaction of **17** (0.5 g, 1.506 mmol) with p-toluenesulphonyl chloride (0.345 g, 1.80 mmol) gave 0.140 g (30%) of **20** as an orange-red solid.

M.p. 180°–182°C. IR (KBr): $\nu = 3400$, 3000, 1500, 1450, 1390, 1320, 1100 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 6.57$ (s, 1H, NH, D_2O exchangeable), 6.80 (d, 2H, J = 9.16 Hz, Ar-H), 7.59–7.86 (m, 6H, Ar-H), 8.0–8.12 (m, 3H, Ar-H), 8.69–8.80 (m, 2H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$, DEPT-90): $\delta = 128.32$, 127.48, 127.29, 127.18, 126.92, 126.33, 123.48, 123.04, 122.74, 122.55, 113.64. Anal. calc. for $C_{20}H_{14}N_2O_2$: C, 76.41; H, 4.49; N, 8.91. Found: C, 76.0; H, 4.80; N, 9.01.

(+)trans-1,2-Dimethyl-3-phenylaziridine (**21**) and (1R,2S)-2-[N-Methyl-(4-toluenesulphonyl)-amino]-1-phenylpropan-1-ol (**22**)

Following the general procedure, treatment of L-ephedrine (0.5 g, 3 mmol) with p-toluene sulphonylchloride (0.690 g, 3.63 mmol) gave the expected (+)trans 1,2-dimethyl-3-phenyl aziridine **21** 0.090 g (20%) as a viscous liquid, along with 0.675 g (70%) of **22** as the major product. The IR and NMR data of **21** agreed with the reported data.[33]

Compound 22

M.p. 124°–126°C. IR (KBr): $\nu = 3550$, 3090, 3020, 3000, 2950, 1590, 1370, 1320, 1150, 1120, 1100, 890 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (d, 3H, N-CH_3), 2.38 (s, 3H, Ar-CH_3), 2.68 (s, 3H, Ar-CH_3), 4.14 (dq, 1H, -CH-), 4.80 (d, 1H, Ar-CH), 7.25 (d, 2H, J = 7.8 Hz, Ar-H), 7.30–7.35 (m, 5H, Ar-H), 7.55 (d, 2H, J = 8.3 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 10.85$ (q), 21.45 (q), 30.42 (q), 57.88 (d), 76.74 (d), 126.20 (d), 127.0 (d), 127.60 (s), 128.25 (s), 129.61 (d), 136.29 (d), 141.60 (s), 143.12 (s). Anal calc. for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.63; N, 4.38. Found: C, 63.50; H, 6.59; N, 4.42. Further the structure of the compound **22** has been confirmed by XRD.[34]

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