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Ring opening reactions of 1-arenesulfonyl-2-(bromomethyl)aziridines

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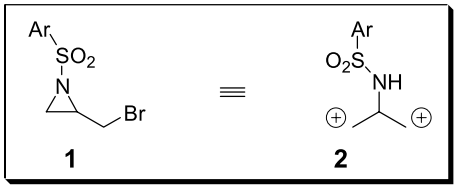
Abstract—The reactivity of 1-arenesulfonyl-2-(bromomethyl)aziridines with respect to lithium dialkylcyanocuprates and lithium dialkylcuprates (Gilman reagents) has been evaluated for the first time, pointing to the conclusion that these substrates can be applied successfully as synthetic equivalents for the 2-aminopropane dication synthon towards 2-alkylaziridines and α-branched *N*-tosylamides in good yields.

1. Introduction

In the past decade, many efforts have been devoted to the implementation of aziridines in synthetic organic chemistry, complementary to the yet well-established epoxide chemistry. An interesting feature of these constrained heterocycles concerns ring opening towards a large variety of functionalized amines, depending on the choice of the appropriate nucleophile.[1] It has been generally acknowledged that N-activation of aziridines augments the facility for ring opening by nucleophilic attack and, consequently, a variety of N-activated aziridines have been studied in the literature. Among others,[2] the arenesulfonyl group has proven to be a very suitable activating group, hence the interest in *N*-(arenesulfonyl)aziridines for a variety of synthetic protocols.[3] 1-Arenesulfonyl-2-(bromomethyl)-aziridines **1**[4] constitute a peculiar subclass of these activated aziridines due to the presence of three electrophilic centres, namely the two carbon atoms of the aziridine moiety and the exocyclic methylene group. In this report, the applicability of these hitherto scarcely reported 2-(bromomethyl)aziridines in ring opening reactions with lithium cuprate reagents is disclosed, allowing selective synthesis of 2-alkylaziridines and α-branched *N*-tosylamides depending on the amount of reagent used. In this way, these substrates can be seen as useful synthetic equivalents for the 2-aminopropane dication synthon **2**, in close relationship with the very recently published dication equivalence of *N*,*O*-bis(diphenylphosphinyl)hydroxymethylaziridine in ring opening reactions with copper(I)-modified Grignard reagents.[2d]



1 **2**

2. Results and discussion

1-Arenesulfonyl-2-(bromomethyl)aziridines **1** are very easily accessible, and thus very attractive, starting materials for organic synthesis.[4] 1-Tosyl-2-(bromomethyl)aziridine **1a** and 1-benzenesulfonyl-2-(bromomethyl)aziridine **1b** were prepared from allylamine in a very efficient two-step procedure adapted from the literature (Scheme 1).[5] First, allylamine **3** was treated with 1.1 equiv. of hydrobromic acid and subsequently with 1.5 equiv. of bromine in water, resulting in 1-amino-2,3-dibromopropane hydrobromide **4** in 86% yield after stirring for 4 h at room temperature. Second, treatment of this ammonium salt with 1.05 equiv. of arenesulfonyl chloride in aqueous sodium hydroxide (2.5 M) afforded the desired 2-(bromomethyl)aziridines **1** after 1 h stirring at room temperature.

In the next stage, the reactivity of these 1-arenesulfonyl-2-(bromomethyl)aziridines **1** with respect to lithium cuprate reagents was evaluated. The synthetic potential of these organocuprates explains the general interest in these sources of carbon-centered nucleophiles as alternatives for conventional organometallic reagents.[6] Treatment of 1-tosyl-2-(bromomethyl)aziridine **1a** with 1.05 equiv. of a lithium dialkylcyanocuprate in THF or diethyl ether furnished the

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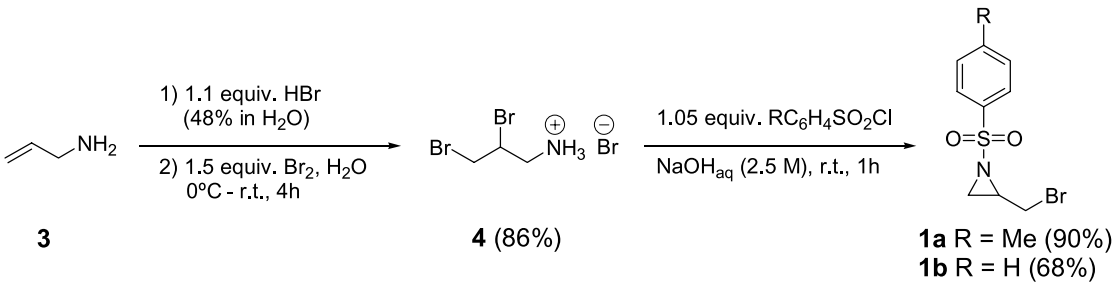
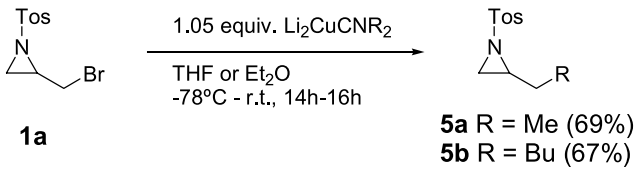


Scheme 1.



Scheme 2.

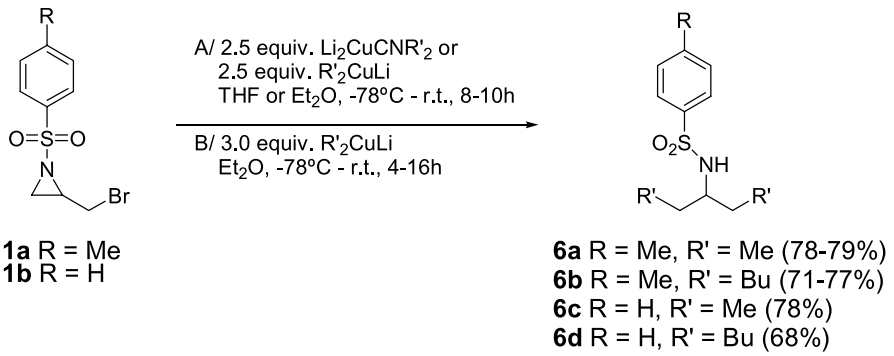
corresponding 2-substituted alkylaziridines **5** in good yield after 14–16 h stirring at room temperature (Scheme 2).

The observation that this transformation was very straightforward allowed to reject the possibility that the nucleophile might react at least as rapidly with the newly formed aziridines as with the starting material. In that case also acyclic amines would be present in the reaction mixture, besides some unreacted starting material.

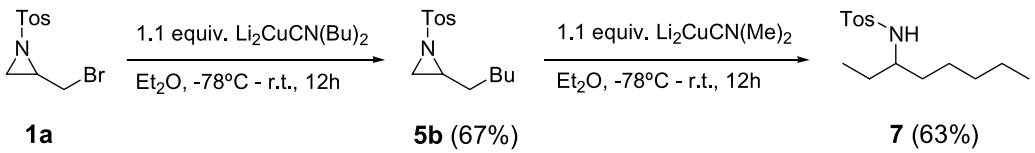
It had already been demonstrated in the literature that the closely related 1-tosyl-2-(tosyloxymethyl)aziridines exhibit a similar reactivity upon treatment with organocuprate reagents.[7] These substrates suffer ring opening by attack at the least hindered carbon atom of the aziridine moiety, immediately followed by ring closure by displacement of the tosylate in a straightforward manner.[7] Also for *N*,*O*-bis(diphenylphosphinyl)-2-(hydroxymethyl)aziridine comparable results were published, although in this case the reaction with some copper(I)-modified Grignard reagents gave rise to the formation of a side product, namely 1-diphenylphosphinyl-2-(bromomethyl)aziridine, up to 25%.[2d]

1-Arenesulfonyl-2-(bromomethyl)aziridines **1** also provide an easy access to symmetrical sulfonamides, simply be increasing the amount of lithium cuprate reagent. When 1-tosyl-2-(bromomethyl)aziridine **1a** was treated with 2.5 equiv. of lithium dialkylcyanocuprate, or alternatively, with 2.5 equiv. of lithium dialkylcuprate (Gilman reagent) in THF or in diethyl ether at room temperature, the corresponding ring opened symmetrical sulfonamides **6a**-**b** were isolated in good yields (Scheme 3). 1-Benzenesulfonyl-2-(bromomethyl)aziridine **1b** was easily converted into the sulfonamides **6c**-**d** in a similar way upon treatment with 3 equiv. of Gilman reagent in diethyl ether after 4 or 16 h stirring at room temperature (Scheme 3). Comparable observations were described for the reaction of *N*,*O*-bis-(diphenylphosphinyl)-2-(hydroxymethyl)aziridine with copper(I)-modified Grignard reagents, that is, different alkyl and aryl magnesium bromides in the presence of 5 mol% $CuBr{\cdot}SMe_2$.[2d]

The different intrinsic reactivity of 1-arenesulfonyl-2-(bromomethyl)aziridines and 1-arenesulfonyl-2-alkylaziridines with respect to organocuprate reagents paved the way for the selective synthesis of an unsymmetrical amine **7** (Scheme 4). When 1-tosyl-2-pentylaziridine **5b**, prepared



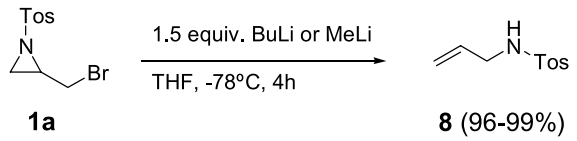
Scheme 3.



Scheme 4.

from 1-tosyl-2-(bromomethyl)aziridine **1a** upon treatment with 1.1 equiv. of lithium dibutylcyanocuprate in Et_2O, was treated with 1.1 equiv. of lithium dimethylcyanocuprate in Et_2O, the desired *N*-(1-ethylhexyl)tosylamide **7** was isolated in 63% yield as a single reaction product (Scheme 4).

Attempts to replace the lithium cuprates by alkyllithium reagents for the delivery of carbon-centered nucleophiles were unsuccessful. Instead, when 1-tosyl-2-(bromomethyl)-aziridine **1a** was treated with 1.5 equiv. of butyllithium or methyllithium in THF at −78 °C for 4 h, metal-halogen exchange resulted in *N*-(allyl)tosylamide **8** due to ring opening of the aziridine (Scheme 5).



Scheme 5.

3. Conclusion

1-Arenesulfonyl-2-(bromomethyl)aziridines are convenient synthetic equivalents for the 2-aminopropane-1,3-dication synthon. Depending on the amount of lithium cuprate used, these aziridines were successfully transformed into 2-alkyl-aziridines and symmetrical α-branched *N*-tosylamides in a good yield, with either 1 or at least 2 equiv. of reagent, respectively. Also an unsymmetrical amine was prepared by consecutive treatment of 1-tosyl-2-(bromomethyl)aziridine with 1 equiv. of two different lithium cuprate reagents. As plentiful methods exist for the N-detosylation of *N*-tosylamides,[8] the presented methodology offers a suitable access to the synthesis of the corresponding amines.

4. Experimental

^{1}H NMR spectra were recorded at 270 MHz (JEOL JNM-EX 270) with $CDCl_3$ as solvent and tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded at 68 MHz (JEOL JNM-EX 270) with $CDCl_3$ as solvent. Mass spectra were obtained with a mass spectrometer (VARIAN MAT 112, 70 eV) using a GC–MS coupling (RSL 200, 20 m glass capillary column, i.d. 0.53 mm, He carrier gas). IR spectra were measured with a Perkin–Elmer 1310 spectrophotometer or a Spectrum One FT-IR spectrophotometer. Dichloromethane was distilled over calcium hydride, and diethyl ether and THF were dried by distillation over sodium benzophenone ketyl. Other solvents were used as received from the supplier.

4.1. Synthesis of 1-arenesulfonyl-2-(bromomethyl)-aziridines 1 (Adapted from the literature)[5]

To an ice-cooled, stirred solution of allylamine **3** (8.57 g, 150 mmol) in water (50 mL), hydrobromic acid (27.81 g, 165 mmol, 1.1 equiv., 48% in H_2O) was added dropwise, followed by the addition of a solution of bromine (35.96 g, 225 mmol, 1.5 equiv.) in water (50 mL) at 0 °C, and the mixture was further stirred for 4 h at room temperature. Evaporation of the solvent in vacuo and recrystallisation from methanol afforded 1-amino-2,3-dibromopropane hydrobromide **4** (38.42 g, 86% yield) as white crystals. Subsequently, 1-amino-2,3-dibromopropane hydrobromide **4** (29.78 g, 100 mmol) was dissolved in water (100 mL), followed by the addition of arenesulfonyl chloride (105 mmol, 1.05 equiv.) at room temperature. Finally, a sodium hydroxide solution (100 mL, 5 M in H_2O) was added under vigorous stirring at room temperature, followed by a stirring period of 1 h at room temperature. Extraction with dichloromethane (3×75 mL), washing with brine (1×100 mL), drying ($MgSO_4$), filtration and evaporation of the solvent in vacuo afforded 1-arenesulfonyl-2-(bromomethyl)aziridine **1**.

The spectral data of 1-tosyl-2-(bromomethyl)aziridine **1a** have been reported previously in the literature.[4b] No full spectroscopic data of 1-benzenesulfonyl-2-(bromomethyl)-aziridine **1b** have been reported up to now, therefore they are reported here.

4.1.1. 1-Benzenesulfonyl-2-(bromomethyl)aziridine 1b. Yield 68%, white crystals. Mp 83.4–84.5 °C, recrystallisation from ethanol. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.22 (1H, d, J=5.0 Hz, (H_{trans}CH)N); 2.81 (1H, d, J=6.5 Hz, (HCH_{cis})N); 3.09–3.16 (1H, m, CHN); 3.31 (2H, d, J=7.8 Hz, CH_2Br); 7.41–8.06 (5H, m, C_6H_5). ^{13}C NMR (68 MHz, $CDCl_3$): δ 30.55 (CH_2N); 34.34 (CH_2Br); 39.96 (CHN); 128.19 and 129.11 (2×HC$_{ortho}$ and 2×HC$_{meta}$); 133.92 (HC$_{para}$); 137.37 (C$_{arom,quat}$). IR (NaCl, cm^{-1}): ν= 1583, 1446, 1321, 1174. MS (70 eV) *m*/*z* (%): 275/7 (M^+, 2); 196 (90); 141 (82); 136 (91); 134 (93); 77 (100). Anal. Calcd for $C_9H_{10}BrNO_2S$: C 39.14%; H 3.65%; N 5.07%. Found: C 39.31%; H 3.78%; N 4.91%.

4.2. Synthesis of 1-(4-methylbenzenesulfonyl)-2-alkyl-aziridines 5

As a representative example, the synthesis of 1-tosyl-2-ethylaziridine **5a** is described. To a solution of copper cyanide (0.25 g, 2.7 mmol, 1.05 equiv.) in dry diethyl ether (45 mL), methyllithium (3.4 mL, 5.4 mmol, 2.1 equiv., 1.6 M in ether) was added dropwise via a syringe at −78 °C and under nitrogen atmosphere, and the resulting mixture was stirred for 30 min at −78 °C. Subsequently, a solution of 1-tosyl-2-(bromomethyl)aziridine **1a** (0.74 g, 2.6 mmol) in diethyl ether (10 mL) was added at −78 °C, after which the mixture was stirred for 12 more hours at room temperature. The reaction mixture was then filtered over Celite®, and the filtrate was extracted with a saturated $NaHCO_3$ solution and ether (3×50 mL). Drying ($MgSO_4$), filtration and evaporation in vacuo afforded 1-(4-methyl-benzenesulfonyl)-2-ethylaziridine **5a** (0.40 g, 69%).

4.2.1. 1-(4-Methylbenzenesulfonyl)-2-ethylaziridine 5a. Yield 69%, colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.83 (3H, t, J=7.6 Hz, CH_3CH$_2$); 1.07–1.61 (2H, m, CH$_3$CH_2); 2.07 (1H, d, J=4.3 Hz, (H_{trans}CH)N); 2.44 (3H, s, CH_3Ar); 2.62 (1H, d, J=7.3 Hz, (HCH_{cis})N); 2.63–2.71 (1H, m, CHN); 7.33 and 7.82 (4H, 2×d, J=7.9 Hz, 2×HC$_{ortho}$ and 2×HC$_{meta}$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 10.84 (*C*H$_3$CH$_2$); 21.64 (*C*H$_3$Ar); 24.47 (CH$_3$*C*H$_2$); 33.58 (CH_2N); 41.71 (CHN); 127.98 and 129.63 (2×HC$_{ortho}$ and 2×HC$_{meta}$); 135.16 (CH$_3$*C*$_{arom,quat}$); 144.42 (C$_{arom,quat}$). IR

(NaCl, cm^{-1}): ν=1672, 1591, 1460, 1319, 1228, 1157, 1086, 1026. MS (70 eV) *m/z* (%): 225 (M^+, 0.5); 197 (1); 155 (4); 91 (24); 70 (100); 65 (14); 51 (3). Anal. Calcd for $C_{11}H_{15}NO_2S$: C 58.64%; H 6.71%; N 6.22%. Found: C 58.77%; H 6.85%; N 6.13%.

4.2.2. 1-(4-Methylbenzenesulfonyl)-2-pentylaziridine 5b. Yield 67%, colorless liquid. ^1H NMR (270 MHz, $CDCl_3$): δ 0.81 (3H, t, J=5.9 Hz, CH_3CH_2); 1.11–1.56 (8H, m, $CH_3(CH_2)_4$); 2.05 (1H, d, J=4.3 Hz, (H_{trans}CH)N); 2.42 (3H, s, CH_3Ar); 2.62 (1H, d, J=6.9 Hz, (HCH_{cis})N); 2.65–2.72 (1H, m, CHN); 7.32 and 7.82 (4H, 2×d, J=8.0 Hz, 2×HC_{ortho} and 2×HC_{meta}). ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.84 (CH_3CH_2); 21.58 (CH_3Ar); 22.43, 26.43, 31.16 and 31.27 ($CH_3(CH_2)_4$); 33.75 (CH_2N); 40.48 (CHN); 127.99 and 129.61 (2×HC_{ortho} and 2×HC_{meta}); 135.20 ($CH_3C_{arom,quat}$); 144.44 ($C_{arom,quat}$). IR (NaCl, cm^{-1}): ν=2931, 2863, 1598, 1465, 1324, 1240, 1154. Anal. Calcd for $C_{14}H_{21}NO_2S$: C 62.89%; H 7.92%; N 5.24%. Found: C 63.04%; H 8.11%; N 5.12%.

4.3. Synthesis of tosylamides 6

As a representative example, the synthesis of *N*-(1-ethylpropyl)-4-methylbenzenesulfonamide **6a** is described. To a solution of copper iodide (0.99 g, 5.2 mmol, 3 equiv.) in dry diethyl ether (35 mL), methyllithium (6.5 mL, 10.4 mmol, 6 equiv., 1.6 M in ether) was added dropwise via a syringe at −78 °C and under nitrogen atmosphere, and the solution was further stirred for 30 min at −78 °C. Subsequently, a solution of 1-(4-methylbenzenesulfonyl)-2-(bromomethyl)-aziridine **1a** (0.50 g, 1.7 mmol) in diethyl ether (5 mL) was added at −78 °C, after which the mixture was stirred for 5 more hours at room temperature. The reaction mixture was then filtered over Celite®, and the filtrate was extracted with water and ether (3×50 mL). Drying ($MgSO_4$), filtration and evaporation in vacuo afforded *N*-(1-ethylpropyl)-4-methylbenzenesulfonamide **6a** (0.32 g, 79%).

4.3.1. *N*-(1-Ethylpropyl)-4-methylbenzenesulfonamide 6a. Yield 79%, colorless liquid. Flash chromatography on silica gel: Acetone/chloroform (1:1), R_f=0.70. ^1H NMR (270 MHz, $CDCl_3$): δ 0.71 (6H, t, J=7.3 Hz, ($CH_3CH_2)_2$); 1.21–1.45 (4H, m, ($CH_3CH_2)_2$); 2.37 (3H, s, CH_3Ar); 3.01–3.09 (1H, m, CHN); 4.94 (1H, br s, NH); 7.24 and 7.74 (4H, 2×d, J=8.2 Hz, 2×HC_{ortho} and 2×HC_{meta}). ^{13}C NMR (68 MHz, $CDCl_3$): δ 9.61 (($CH_3CH_2)_2$); 21.49 (CH_3Ar); 27.15 (($CH_3CH_2)_2$); 56.69 (CHN); 126.99 and 129.52 (2×HC_{ortho} and 2×HC_{meta}); 138.59 ($CH_3C_{arom,quat}$); 142.98 ($C_{arom,quat}$). IR (NaCl, cm^{-1}): ν=3350, 3287, 1596, 1456, 1413, 1327, 1157. MS (70 eV) *m/z* (%): no M^+; 155 (1); 123 (4); 121 (13); 119 (15); 88 (52); 86 (94); 84 (100); 51 (21); 49 (83); 47 (77). Anal. Calcd for $C_{12}H_{19}NO_2S$: C 59.72%; H 7.93%; N 5.80%. Found: C 59.88%; H 8.10%; N 5.74%.

4.3.2. *N*-(1-Pentylhexyl)-4-methylbenzenesulfonamide 6b. Yield 77%, colorless liquid. ^1H NMR (270 MHz, $CDCl_3$): δ 0.81 (6H, t, J=6.6 Hz, 2×CH_3CH_2); 1.05–1.39 (16H, m, 2×($CH_3(CH_2)_4$)); 2.41 (3H, s, CH_3Ar); 3.17–3.19 (1H, m, CHN); 4.57 (1H, br d, J=8.3 Hz, NH); 7.28 and 7.41 (4H, 2×d, J=8.0 Hz, 2×HC_{ortho} and 2×HC_{meta}). ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.93 (2×CH_3CH_2); 21.46 (CH_3Ar); 22.46, 24.89, 31.55 and 35.02 (2×($CH_3(CH_2)_4$)); 54.14 (CHN); 127.06 and 129.50 (2×HC_{ortho} and 2×HC_{meta}); 138.54 ($CH_3C_{arom,quat}$); 143.03 ($C_{arom,quat}$). IR (NaCl, cm^{-1}): ν=3277, 2936, 2853, 1598, 1457, 1423, 1324, 1153. MS (70 eV) *m/z* (%): 326 (M^+, 1); 255 (74); 184 (5); 171 (8); 155 (62); 147 (5); 139 (4); 107 (5); 91 (100); 77 (3); 65 (24); 56 (28). Anal. Calcd for $C_{18}H_{31}NO_2S$: C 66.42%; H 9.60%; N 4.30%. Found: C 66.58%; H 9.76%; N 4.21%.

4.3.3. *N*-(1-Ethylpropyl)benzenesulfonamide 6c. Yield 78%, colorless liquid. Flash chromatography on silica gel: Acetonitrile/Chloroform (1/1), R_f=0.75. ^1H NMR (270 MHz, $CDCl_3$): δ 0.75 (6H, t, J=7.4 Hz, ($CH_3CH_2)_2$); 1.26–1.56 (4H, m, ($CH_3CH_2)_2$); 3.08–3.16 (1H, m, CHN); 4.82 (1H, br d, J=7.9 Hz, NH); 7.47–7.62 (3H, m, 2×HC_{meta} and HC_{para}); 7.89–7.98 (2H, m, 2×HC_{ortho}). ^{13}C NMR (68 MHz, $CDCl_3$): δ 9.61 (($CH_3CH_2)_2$); 27.19 (($CH_3CH_2)_2$); 56.78 (CHN); 126.90 and 128.95 (2×HC_{ortho} and 2×HC_{meta}); 132.36 (HC_{para}); 141.42 ($C_{arom,quat}$). IR (NaCl, cm^{-1}): ν=3275, 1450, 1312, 1164. MS (70 eV) *m/z* (%): 227 (M^+, 0.2); 198 (100); 141 (48); 77 (41); 51 (9). Anal. Calcd for $C_{11}H_{17}NO_2S$: C 58.12%; H 7.54%; N 6.16%. Found: C 58.20%; H 7.68%; N 6.05%.

4.3.4. *N*-(1-Pentylhexyl)benzenesulfonamide 6d. Yield 68%, colorless liquid. Flash chromatography on silica gel: EtOAc/Hexane (1/1), R_f=0.42. ^1H NMR (270 MHz, $CDCl_3$): δ 0.81 (6H, t, J=6.9 Hz, 2×CH_3); 1.11–1.42 (16H, m, 2×($CH_3(CH_2)_4$)); 3.17–3.25 (1H, m, CHN); 5.02 (1H, br d, J=8.2 Hz, NH); 7.29–7.92 (5H, m, C_6H_5). ^{13}C NMR (68 MHz, ref=$CDCl_3$): δ 13.86 (2×CH_3); 22.36, 24.80, 31.45 and 34.88 (2×($CH_3(CH_2)_4$)); 54.16 (CHN); 126.88 and 128.81 (2×HC_{ortho} and 2×HC_{meta}); 132.18 (HC_{para}); 141.46 ($C_{arom,quat}$). IR (NaCl, cm^{-1}): ν=3282, 1587, 1448, 1325, 1162. MS (70 eV) *m/z* (%): 311 (M^+, 0.1); 240 (100); 170 (9); 141 (33); 77 (36); 51 (4). Anal. Calcd for $C_{17}H_{29}NO_2S$: C 65.55%; H 9.38%; N 4.50%. Found: C 65.75%; H 9.49%; N 4.40%.

4.3.5. Synthesis of *N*-(1-ethylhexyl)-4-methylbenzenesulfonamide 7. This compound was prepared in a two-step procedure starting from 1-(4-methylbenzenesulfonyl)-2-(bromomethyl)aziridine **1a** via 1-(4-methylbenzenesulfonyl)-2-pentylaziridine **5b**, analogous to the procedures described above.

Yield 63%, colorless liquid. ^1H NMR (270 MHz, $CDCl_3$): δ 0.75–0.84 (6H, m, 2×CH_3); 1.12–1.49 (10H, m, (CH_3CH_2-$CH(CH_2)_4CH_3$); 2.42 (3H, s, CH_3Ar); 3.27–3.33 (1H, m, CHN); 4.81 (1H, br s, NH); 7.29 and 7.79 (4H, 2×d, J=7.2, 8.2 Hz, 2×HC_{ortho} and 2×HC_{meta}). ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.94 (2×CH_3); 21.47 (CH_3Ar); 22.46 (2×CH_3CH_2); 24.89 ($CH_3CH_2CH_2$); 31.55 ($CH_3(CH_2)_2$-CH_2); 34.92 ($CH_3(CH_2)_3CH_2$); 55.35 (CHN); 127.04 and 129.50 (2×HC_{ortho} and 2×HC_{meta}); 138.56 ($CH_3C_{arom,quat}$); 143.00 ($C_{arom,quat}$). IR (NaCl, cm^{-1}): ν=3282, 1599, 1494, 1455, 1429, 1326, 1157, 1094, 1031. MS (70 eV) *m/z* (%): no M^+; 212 (5); 166 (4); 140 (4); 126 (35); 112 (8); 97 (12); 86 (16); 85 (61); 84 (13); 71 (100); 69 (13); 57 (98); 55 (19). Anal. Calcd for $C_{15}H_{25}NO_2S$: C 63.56%; H 8.89%; N 4.94%. Found: C 63.68%; H 9.02%; N 4.91%.

Acknowledgements

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