A New Synthesis of 2-Methyleneaziridines

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A new synthetic route leading to 2-methyleneaziridines has been developed by base-induced 1,2-dehydrobromination of 2-(bromomethyl)aziridines. Several base-solvent pairs did not lead to 2-methyleneaziridines. Only potassium tert-butoxide in tetrahydrofuran afforded 2-methyleneaziridines in competition with the substitution products, i.e., 2-(tert-butoxymethyl)aziridines. Various attempted functionalizations of 1-(arylmethyl)-2-methyleneaziridines failed, but they proved to be excellent substrates for the synthesis of β-lactam derivatives, i.e., 1-(arylmethyl)-2-iminoazetidines, through ring expansion with azides carrying electron-withdrawing substituents.

Introduction

2-Methyleneaziridines 2 belong to a rare class of highly strained heteromethylenecyclopropanes, which caught a lot of interest in view of their potential to give valence isomerizations. There are only a few synthetic routes leading to 2-methyleneaziridines, the most general one being the cyclization of 2-bromo-2-propenylamines 1 with sodium amide in liquid ammonia1 being the cyclization of 2-bromo-2-propenylamines leading to 2-methyleneaziridines, the most general one isomerizations. There are only a few synthetic routes in very low yield (3–8%),6 while the synthesis of a highly functionalized 2-(bromomethylene)aziridine via electro-bromination of 1-acetoxy-4-(N-acetylamino)-4-methyl-1-phenyl-2-pentyne has to be considered as an exceptional case. Some 2-methyleneaziridines have been postulated as intermediates, for instance during the rearrangement of 2-chloro-2-methylaziridines with potassium tert-butoxide4 or during the cycloaddition of phthalimido tosylate8 or during the cycloaddition of phthalimido-nitrene40 as intermediates, for instance during the rearrangement with organic azides.8 The protonation at nitrogen of 2-methyleneaziridines in superacid medium with and without ring rupture has been studied.16,17 A major feature of 2-methyleneaziridines is their propensity to give a valence isomerization to afford an isomeric (if not degenerated) methyleneaziridine and a cyclopropylidenemaine, the latter usually fragmenting into an olefin and an isonitrile.11,18,19

An obvious and straightforward entry to 2-methyleneaziridines 2 would be the 1,2-dehydrobromination of 2-(bromomethyl)aziridines 4, which became recently accessible via reductive ring closure of N-arylidene-2,3-dibromopropylamines.20,21 In the present report, the 1,2-dehydrobromination of 2-(bromomethyl)aziridines 4 was investigated, and the resulting 2-methyleneaziridines were converted into 2-iminoazetidines by skeletal rearrangement with organic azides.

Results and Discussion

2-(Bromomethyl)aziridines 7 are accessible from aldehydes 5 in three high yielding steps. Condensation of

proteinase K, 10 μg; N-acetylserine, 20 μM; and L-serine, 50 μM. After 30 min, the reaction was stopped by addition of a stop solution containing 30% acetic acid and 0.5% 5-bromo-4-chloro-3-indolyl phosphate (BCIP) in 100 mM NaH2PO4, pH 7.8. The plates were washed with 50 mM NaCl, 100 mM NaH2PO4, pH 7.8, and stained with 1% Coomassie blue in 10% methanol and 10% acetic acid. The absorbance of the stained bands was determined at 670 nm using a spectrophotometer.
aldehydes 5 with allylamine in dichloromethane in the presence of magnesium sulfate as drying agent affords the corresponding N-allylamine which react smoothly with bromine in dichloromethane to give rise to N-(arylidene)-2,3-dibromopropylamines 6. The latter dibromomines react with sodium borohydride in methanol under reflux to produce 2-(bromomethyl)aziridines 7 in 35–85% yield (Scheme 2). 2-(Bromomethyl)aziridines 7 are a class of rare and relatively unreactive β-bromo amines. Only one 2-(bromomethyl)aziridine, i.e. the N-tert-butyldimethylsilyl derivative, was reported and was obtained from the reaction of 1-tert-butyl-2-[p-tosyloxymethyl]-aziridine with tetrabutylammonium bromide. Only a very few related 2-(chloromethyl)aziridines are accessible either by ring opening of epichlorohydrin with tert-butylamine or cyclohexylamine and subsequent ring closure, or by rearrangement of 1-tert-butyl-2-(diphenylhydroxymethyl)aziridine with thionyl chloride in the presence of sodium hydride.

In order to find suitable conditions for the transformation of 4 into 2, the model compound 1-benzyl-2-(bromomethyl)aziridine (7a) (R = C₆H₅) was treated with several bases under a variety of conditions. Lithium diisopropylamine or sodium hydride in THF at room temperature for 22 h did not convert 2-(bromomethyl)aziridine 7a into 2-methyleneaziridine 8a. Sodium hydride in benzene did not dehydrobrominate compound 7a. The temperature had a major outcome on the reaction of 7a with sodium hydride in dimethyl sulfoxide (DMSO). The dimethyl anion in DMSO did not dehydrobrominate compound 7a at room temperature (29 h), while a complete consumption but no 2-methyleneaziridine formation was observed at 100–135 °C. No products could be identified from the complex reaction mixture. Various experiments of compound 7a with the dimethyl anion in DMSO at 45–50 °C during one to three days afforded reaction mixtures containing 20–40% of 2-methyleneaziridine 8a, contaminated with several unidentified products. These intractable mixtures were not investigated further. DBU in DMSO at room temperature (65 h) or DBU in benzene under reflux (7 h) gave either no reaction or a complex reaction mixture without any sign of 2-methyleneaziridine 8a, respectively. Also dichloroethylaluminum in toluene at room temperature for 45 min gave no access to 2-methyleneaziridines. In view of the known behavior of 2-(chloromethyl)aziridines to give nucleophilic substitution with alkoxides in the corresponding alcohol, it was no surprise to observe this substitution reaction with compound 7a and sodium methoxide in methanol or sodium ethoxide in ethanol. The reaction mixtures did not contain a trace of the methyleneaziridine. The reaction of potassium 2,6-di-tert-butyl-4-methylphenoxide in THF at room temperature (15 h) or potassium tert-butoxide in tert-butanol at room temperature (7 h) did not afford a trace of 2-methyleneaziridine 8a. On the other hand, the reaction of compound 7a with potassium tert-butoxide in tert-butyl alcohol under reflux (3 h) produced a reaction mixture in quantitative yield consisting of 20% 2-methyleneaziridine 8a and 80% 2-(tert-butoxymethyl)aziridine 9a. The best base-solvent pair proved to be potassium tert-butoxide (1.5 equiv) in THF, affording a nearly quantitative yield of reaction products 8a and 9a in a ratio of 1:1 at room temperature (24 h). Lowering the temperature to 0 °C or –20 °C resulted in a very slow reaction (3 days) leading to roughly the same 1:1 ratio of 8a and 9a, but with the unappealing presence of 10% (0 °C) or 70% (–20 °C, 3 days) of starting material. The reaction of aziridine 7a with the more sterically hindered potassium tert-butoxide (1.5 equiv) in THF for 12 h under reflux gave also substantial amounts of the substitution product, i.e. 1-benzyl-2-[(tert-butoxymethyl]-aziridine 9c (21%) alongside with a low isolated yield of 11% of 2-methyleneaziridine 8a. When potassium 2,3,4-trimethyl-3-pentoxide was used as a base in THF the only reactivity observed was decomposition of the starting material due to prolonged reaction times. The above selected reaction conditions (KOT-Bu, THF, 24 h, rt) were applied to three other substrates 7, namely 7b (R = 4-MeC₆H₄), 7c (R = 4-ClC₆H₄) and 7d (R = C₂Me₃CH₂C₆H₅), each giving the same 1:1 ratio of 2-methyleneaziridine 8b–d and 2-(tert-butoxymethyl)aziridine 9b–d. The 2-methyleneaziridines 8a–d were isolated by high vacuum distillation affording yields of 40–48%. The 2-(tert-butoxymethyl)aziridines 9a–d were isolated by high vacuum distillation or flash chromatography (silica gel; hexane: ethyl acetate). Attempts to isolate 2-methyleneaziridines 8 by flash chromatography failed completely. During the high vacuum distillation of the 1:1 mixture of 8a and 9a, a small portion (~5–10%) of N-benzylidene-1-propenylamine (mixture of E- and Z-isomers) was isolated in a few cases. Although speculative, this 2-aza-1,3-diene could originate from rupture of the N−C(2) bond of 8a followed by isomerization into the putative N-allyl-N-benzylamine, which subsequently can tautomerize to a 1-azaazidine and further isomerize into the more conjugated 2-azaazidine.

Some efforts were performed to functionalize or transform 2-methyleneaziridines 8. However, the peculiar nature of these strained cyclic enamines prevented them of giving defined reaction products from reactions with m-chloroperbenzoic acid in dichloromethane (−50 °C → rt), acetone cyanohydrin in dichloromethane with or without the presence of catalytic amounts of potassium tert-butoxide (rt or Δ), diazomethane in ether with or without palladium catalysis (rt), N-chlorosuccinimide in carbon tetrachloride (−20 °C → rt) or chlorosulfonfyl isocyanate in ether (−30 °C → rt). No reaction product
The type of carbon was determined either by the DEPT mode or by off resonance decoupled spectra. Mass spectra were measured at 70 eV using a GC-MS coupling or a direct inlet system. Gas chromatographic analyses were performed using a capillary column (fused silica, 20 m, glass capillary column, i.d. 0.53 mm, H₂ carrier gas) or a packed column (5–10% SE-30, Chromosorb W60–80, 1.5 m, H₂ carrier gas).

Synthesis of N-Arylidene-2-propenylamines. A mixture of 0.1 mol of the appropriate aromatic aldehyde 5 in 100 mL of dichloromethane was treated with 0.11 mol of allylamine and 13 g of magnesium sulfate. The mixture was magnetically stirred at room temperature for 1 h and then filtered. After evaporation of the solvent the N-allyl aldimines were distilled in vacuo. N-benzylideneallylamine (84% yield), bp 41–47 °C/0.04 mmHg; N-(4-methylbenzylidene)allylamine (86% yield), bp 68–73 °C/0.05 mmHg; N-(4-chlorobenzylidene)allylamine (90% yield), bp 62–78 °C/0.08 mmHg; N-(2,2-dimethyl-3-phenyl-1-propylidene)allylamine (92% yield), bp 70–76 °C/0.05 mmHg. All aldimines were characterized by ¹H NMR and IR, affording spectral data in agreement with their structure. The purity of these aldimines was checked by GC (> 98%).

Synthesis of N-Arylidene-2,3-dibromopropylamines 6. A stirred and cooled (0 °C) solution of 0.1 mol of N-arylidene-allylamine in 150 mL of dry dichloromethane (freshly distilled from calcium hydride) was treated dropwise with a solution of 0.103 mol of bromine in 30 mL of dichloromethane. After complete addition, stirring was continued at 0 °C for 30 min and the solvent was then evaporated in vacuo to afford the label N-arylidene-2,3-dibromopropylamines 6 in quantitative yield (purity > 95%). Attempted vacuum distillation resulted in total decomposition. These dibromomaldimines 6 were used as such in the next cyclization step.

N-Benzylidene-2,3-dibromopropylamine (6a): ¹H NMR (60 MHz, CCl₄)  δ 3.88 (2H, d, J = 6.8 Hz); 4.0–4.2 (2H, m); 4.2–4.7 (1H, m); 7.3–7.6 (3H, m); 7.6–7.9 (2H, m); 8.33 (1H, s, br). ¹³C NMR (20 MHz, CDCCl₃)  δ 34.0 (s, CH₂Br); 51.1 (d, CHBr); 64.0 (t, CH₂CN); 128.3 and 128.5 (each d, C meso); 133.1 (s, C meso); 163.3 (d, CH = N). IR (NaCl): 1645 cm⁻¹ (C=N). MS m/z (relative intensity): 303/57 (M⁺ + 1); 224/66 (24); 169/71 (24); 149/9 (24); 145/7 (24); 121/12; 119/12; 118/100; 117/10; 106/105; 107/104; 95/92; 91/86; 90/12; 89/12; 77/19; 76/5; 67/5; 63/5; 58/5; 57/5; 51/14; 50/7; 44/3; 43/5; 41/12.

N-(4-Methylenazolidine)-2,3-dibromopropylamine (6b): ¹H NMR (60 MHz, CCl₄)  δ 2.39 (3H, s); 3.87 (2H, d, J = 6.4 Hz); 4.07 (2H, d, J = 4.4 Hz); 4.2–4.7 (1H, m); 7.23 and 6.79 (4H, each d, J = 8 Hz); 8.28 (1H, s, br). ¹³C NMR (20 MHz, CDCCl₃)  δ 21.4 (q, Me); 34.1 (t, CH₂Br); 51.3 (d, CH₂CN); 64.1 (t, CH₂CN); 128.3 and 128.9 (each d, C meso); 133.1 (s, C meso); 141.2 (s, C meso); 163.5 (d, CH = N). IR (NaCl): 1646 cm⁻¹ (C=N). MS m/z (relative intensity): 317/19/21 (M⁺ + 1); 238/40 (Br, 33); 158/6; 132/100; 119/4; 118/8; 117/12; 105/75; 103/8; 99/14; 79/4; 78/4; 77/10; 65/12; 51/4; 44/12.

N-(4-Chlorobenzylidene)-2,3-dibromopropylamine (6c): ¹H NMR (60 MHz, CCl₄)  δ 3.92 (2H, d, J = 7.2 Hz); 4.1–4.3 (2H, m); 4.3–4.8 (1H, m); 7.52 and 7.64 (2 each d, J = 8.8 Hz); 8.40 (1H, s, br). ¹³C NMR (20 MHz, CDCCl₃)  δ 33.9 (d, CH₂CN); 50.6 (d, CH₂CN); 63.3 (d, CH₂CN); 129.1 and 130.1 (each d, C meso); 130.8 and 137.9 (each d, C meso); 163.3 (d, CH = N). IR (NaCl): 1648 cm⁻¹ (C=N). MS m/z (relative intensity): 337/39/41/43 (M⁺ + 1); 263/10; 262/11; 259/61; 258/60; 179/12; 155/15; 154/19; 153/30; 150/15; 151/16; 140/12; 136/13; 128/12; 127/45; 125/15; 122/12; 119/16; 117/14; 116/12; 111/17; 102/14; 90/18; 89/34; 76/15; 75/21; 63/17; 51/15; 50/14; 41/36.

N-(2,2-Dimethyl-3-phenyl-1-propylidene)-2,3-dibromopropylamine (6d): ¹H NMR (60 MHz, CCl₄)  δ 1.03 (6H, s); 2.70 (2H, s); 3.6–3.9 (4H, m); 4.1–4.5 (1H, m); 6.9–7.3 (5H, m); 7.56 (1H, t, J = 1 Hz). ¹³C NMR (20 MHz, CDCCl₃)  δ 24.6 (q, Me₂); 34.0 (t, CH₂Br); 40.4 (s, CMe₂); 46.1 (t, ArCH₂); 51.2 (d, CH₂Br); 63.6 (t, CH₂CN); 126.1 (d, C meso); 127.7 and 130.3 (each d, C meso); 137.7 (s, C meso); 174.6 (d, CH = N). IR (NaCl): 1670 cm⁻¹ (C=N). MS m/z (relative intensity): 359/61/63 (M⁺ + 1); 344/46/48/55; 280/21/15; 199/01/10/13; 186/25; 174/20; 145/30; 144/30; 129/20; 91/100.

Synthesis of 2-(Bromomethyl)aziridines 7a–d. A stirred solution of 0.1 mol of N-arylidene-2,3-dibromopropylamine 6
in 300 mL of absolute methanol was treated portonwise with 0.3 mol of sodium borohydride. After the vigorous reaction ceased, the solution was refluxed for 2 h. The cooled solution was then poured in 500 mL of water, and extraction was performed three times with dichloromethane. The combined extracts were dried (MgSO4) and evaporated in vacuo to give an oil, which consisted mainly of 2-(bromomethyl)aziridine 7 (∼80%). Purification was performed by vacuum distillation affording pure 2-(bromomethyl)aziridine 7 (∼98% H NMR, GC).

1-Benzyl-2-(bromomethyl)aziridine (7a): bp 72–75°C/0.05 mm Hg. % N H NMR (60 MHz, CDCl3) δ 1.3–1.6 (3H, m); 2.77 (3H, s); 2.93 (2H, m); 3.13 and 3.33 (2H, each d, each J = 13 Hz); 7.07 (4H, s). % N C NMR (20 MHz, CDCl3) δ 21.0 (q, each Me); 35.1 and 35.4 (each t, NCH2CH2Br); 40.3 (d, NCH); 63.5 (t, NCH2Ar); 128.0 and 129.0 (each d, c, J = 16 Hz). IR (NaCl): 2964, 1492, 1464, 1371, 1285, 1247, 1217 cm−1 (relative intensity). Anal. Calcd 5.38 N. Found: 5.30 N.

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1-Benzyl-2-(bromomethyl)aziridine (7a) was then poured in 500 mL of water, and extraction was ceased, the solution was refluxed for 2 h. The cooled solution in 300 mL of absolute methanol was treated portionwise with 0.075 mol of sodium borohydride. After the vigorous reaction ceased, the solution was poured in 500 mL of water, and extraction was performed three times with dichloromethane. The combined extracts were dried (MgSO4) and evaporated in vacuo to give an oil. Vacuum distillation of the reaction mixture afforded 40–48% yield of 2-methyleneaziridines 8 and 18% of 2-(bromobutyl)aziridine 9a,b. 2-(bromobutyl)-1-(4-chlorophenyl)methylaziridine 9c was isolated from the residue of distillation by flash chromatography (silica gel; ethyl acetate:hexane 1:4; Rf 0.24, yield 13%) after the corresponding 2-methyleneaziridine 8c had been removed by vacuum distillation.

1-Benzyl-2-methyleneaziridine (8a) bp 46–54°C/0.05 mm Hg. Yield: 40%. % N H NMR (60 MHz, CDCl3) δ 2.06 (2H, t, J = 1 Hz); 3.66 (2H, s); 4.72 (2H, t, J = 1 Hz); 7.34 (5H, s). % N C NMR (20 MHz, CDCl3) δ 30.6 (t, CH2=C=CH2); 62.8 (t, ArCH=N); 83.5 (t, CH=C); 127.3 (d, Cpara); 128.2 and 128.4 (each d, c, J = 10 Hz). IR (NaCl): 1780 cm−1 (C=O). MS m/z (relative intensity): 145 (M+; 11); 144 (33); 111 (105); 94 (110); 77 (11); 65 (33); 54 (44); 39 (16). Anal. Calcd 78.2 C, 7.73 H. Found: 78.27 C, 7.73 H.

1-Benzyl-2-(2-butoxyethyl)-1-(2,2-dimethyl-3-phenylpropyl)aziridine (8b) bp 72–78°C/0.05 mm Hg. Yield: 48%. % N H NMR (270 MHz, CDCl3) δ 2.09 (3H, s); 2.33 (3H, s); 2.64 (2H, s); 4.70 (2H, s); 7.14 and 7.23 (each 2H, each d, J = 7.75 Hz). % N C NMR (68 MHz, CDCl3) δ 21.1 (Me); 30.4 (CH2=CHCH2); 62.5 (ArCH2); 83.4 (CH=C=CH2); 128.2 and 129.1 (Cpara); 135.1, 136.9 and 137.0 (CH2=C2 and 2 × Cpara). IR (NaCl): 1777 cm−1 (C=O). MS m/z (relative intensity): 159 (M+; 9); 158(11); 157 (13); 119(21); 107(27); 61(39); 52(52); 45(44); 41(51). Anal. Calcd 76.67 C, 6.95 H, 6.39 N. Found: 76.81 C, 6.52 H, 6.49 N.

1-Benzyl-2-(2-butoxyethyl)-1-(4-(chlorophenyl)methyl)aziridine (8d) bp 74–80°C/0.05 mm Hg. Yield: 48%. % N H NMR (270 MHz, CDCl3) δ 2.09 (2H, s); 2.33 (3H, s); 2.64 (2H, s); 4.70 (2H, s); 7.14 and 7.23 (each 2H, each d, J = 7.75 Hz). % N C NMR (68 MHz, CDCl3) δ 21.1 (Me); 30.4 (CH2=CHCH2); 62.5 (ArCH2); 83.4 (CH=C=CH2); 128.2 and 129.1 (Cpara); 135.1, 136.9 and 137.0 (CH2=C2 and 2 × Cpara). IR (NaCl): 1777 cm−1 (C=O). MS m/z (relative intensity): 159 (M+; 9); 158(11); 157 (13); 119(21); 107(27); 61(39); 52(52); 45(44); 41(51). Anal. Calcd 76.67 C, 6.95 H, 6.39 N. Found: 76.81 C, 6.52 H, 6.49 N.
1.91 and 2.26 (each 1H, each d, 3.7 Hz); 4.41 (2H, s); 7.27 (5H, s); 7.26 and 7.83 (each 2H, C2452-
(relative intensity): no M
NMR(270MHz,CDCl 3)
9.51 H, 6.96 N. Found: 83.31 C, 9.70 H, 7.10 N.

2-(tert-Butoxymethyl)-1-(2,2-dimethyl-3-phenylprop-
yl)aziridine (9d). Isolated by flash chromatography using silica gel, ethyl acetate/hexane 1:9, Rf 0.22. Yield: 16%. 1H NMR (270 MHz, CDCl3) δ 0.96 (6H, s); 1.21 (9H, s); 1.29 (1H, d, J = 6.27 Hz); 1.55–1.58 (1H, m); 1.65 (1H, d, J = 3.02 Hz); 1.91 and 2.26 (each 1H, each d, J = 12.04 Hz); 2.65 (2H, s, NCH2); 3.23 (1H, d, J = 9.65 Hz, J2 = 5.77 Hz); 3.48 (1H, d × d, J = 9.65 Hz, J2 = 5.77 Hz); 7.16–7.28 (5H, m).

13C NMR (68 MHz, CDCl3) δ 25.5 and 25.6 (Me); 27.6 (Me); 32.5 (NCH2); 36.4 (MeC); 40.0 (NCH); 44.6 (ArCH); 64.9 (CH2O); 71.9 (NCH2C); 72.9 (CO); 125.7 (Cphen); 127.6 and 130.8 (Cphen and Cmeta); 139.3 (Cquat). IR (NaCl): 1467, 1450, 1382, 1360, 1191, 1075 cm−1. MS m/z (relative intensity): 275 (M+)+; 260(4); 218(3); 204(3); 189(8); 188(52); 160(7); 146(11); 143(5); 142(2); 134(1); 129(19); 128(13); 117(12); 115(7); 113(9); 105(14); 97(11); 86(100); 84(12); 72(7); 70(59); 69(14); 68(10); 65(14); 58(12); 57(86); 56(45); 55(32); 54(66); 44(60); 43(41); 42(52); 41(66). Anal. Calcd C 53.95 H 5.09 N. Found: 53.97 C, 4.98 H, 5.09 N.

1-Benzyl-2-(tert-pentoxymethyl)aziridine (9e). Isolated by flash chromatography using silicagel, ethyl acetate/hexane 1:9, Rf 0.16. Yield: 21%. 1H NMR (270 MHz, CDCl3) δ 0.85 (3H, t, J = 7.42 Hz); 1.12 (6H, s); 1.47 (2H, q, J = 7.42 Hz); 1.49 (1H, d, J = 6.27 Hz); 1.72 (1H, d, J = 3.63 Hz); 1.72–1.80 (1H, m); 3.19 and 3.42 (each 1H, each d × d, J = 9.73 Hz, J2 = 5.61 Hz); 3.43 and 3.50 (each 1H, each d, J = 13.86 Hz); 7.26–7.65 (5H, m). 13C NMR (68 MHz, CDCl3) δ 8.2 (MeCH3); 25.0 and 25.1 (MeC); 32.3 and 32.5 (CH2NC6H5 and CHMe); 39.6 (CHN); 64.1 (ArCH2N and CH2O); 74.9 (CO); 126.9 (Cphen); 128.0 and 128.3 (Cphen and Cmeta); 139.3 (Cquat). IR (NaCl): 1463, 1545, 1361, 1179, 1161, 1080 cm−1. MS m/z (relative intensity): no M+; 204 (M+ - Et; 1); 164(6); 163(5); 162(13); 146(14); 133(5); 132(5); 129(11); 72(37); 71(41); 70(8); 65(16); 55(21); 54(5); 51(5); 44(10); 43(65); 42(23); 41(21). Anal. Calcd C60 H60 N0. Found: 58.99 N.

Synthesis of 1-(Arylmethyl)-2-(N-sulfonilyl)iminooz-
azetidines 10 and 11. A mixture of 0.001 mol of 2-methylene-
ziridine 8 and 0.001 mol of p-toluesulfonyl azide or meth-
anesulfonyl azide was heated neat at 80 °C during which nitrogen evolved. The cold reaction mixture was chromatographed over alumina using dichloromethane as eluent affording pure 2-iminoazetidines 10 or 11 in 80–89% yield.

1-Benzyl-2-N-(p-toluenesulfonyl)iminoozazetidine (10a): Rf: 0.39. Yield: 89%. 1H NMR (60 MHz, CDCl3) δ 2.40 (3H, s); 3.27 (2H, t, J = 3.7 Hz); 3.50 (2H, t, J = 3.7 Hz); 4.41 (2H, s); 7.27 (5H, s); 7.26 and 7.85 (each 2H, each d, J = 8 Hz). 13C NMR (20 MHz, CDCl3) δ 21.4 (q, Me); 33.3 (t, CH2NC6H5); 45.6 (t, CH2NC6H5); 48.0 (ArCH2N); 126.4, 128.1, 128.4, 128.9 and 129.3 (each d, Cphen); 133.4 and 140.2 (Cquat); 168.8 (s, C=O). IR (NaCl): 1630 cm−1 (C=O).

1-(4-Chlorophenyl)methyl)-2-N-(p-toluenesulfonyl)-iminoazetidine (11b): Rf: 0.27. Yield: 30%. 1H NMR (270 MHz, CDCl3) δ 3.00 (3H, s); 3.34 (3H, t, J = 3.63 Hz); 3.56 (2H, t, J = 3.63 Hz); 4.41 (2H, s, CH2Ar); 7.22 and 7.35 (each 2H, each d, J = 8.25 Hz). 13C NMR (68 MHz, CDCl3) δ 33.4 (CH3-C=O); 42.3 (MeSO2); 45.8 (CH2NC6H5); 47.3 (ArCH2N); 129.2 and 129.8 (Cphen); 132.6 and 134.1 (Cquat); 168.5 1(C=O). IR (KBr): 1630 cm−1 (C=O).

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