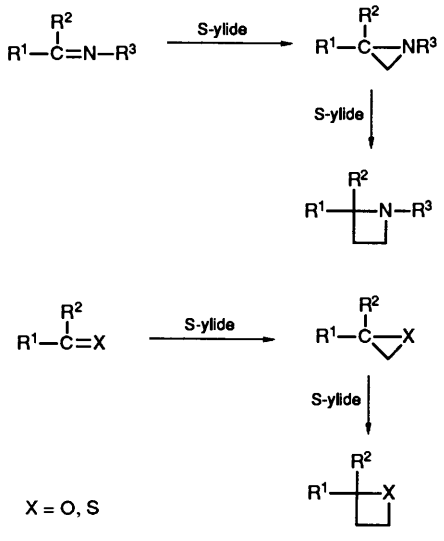
Methylene Transfer from Dimethyloxosulphonium Methylide to *N*-Arylsulphonylaziridines: Stereospecific Synthesis of *N*-Arylsulphonylazetidines

Upender K. Nadir,* Ms. Raman L. Sharma and Veerinder K. Koul
Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110 016, India

Several 2-alkyl-, 2-aryl-, 2-benzyl-, 2,3-dialkyl- and 2,3-diaryl-*N*-arylsulphonylazetidines have been prepared in fair to good isolated yields through reaction of *N*-arylsulphonylaziridines with dimethyloxosulphonium methylide. Fused azetidines, however, could not be obtained through this procedure. The stereospecificity and generality of the reaction together with the ready accessibility of the required aziridines make this methodology attractive. Evidence supporting an addition–1,4-elimination mechanism, rather than one involving intermediacy of an azomethine ylide, is presented.

Sulphur ylides have been used as methylene transfer agents for making cyclopropanes and oxiranes from suitable double bond precursors.[1] To a lesser extent the same procedure has been used to prepare aziridines and thiiranes.[2] Further reaction of the three-membered rings, so formed, with sulphur ylides, which could form an attractive approach to the corresponding four-membered rings (Scheme 1) had been little explored prior

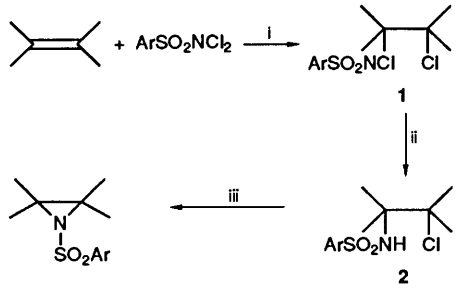


Scheme 1

to our efforts. This is particularly surprising in view of the paucity of general azetidine synthesis.[3] In previous communications[4,5] we have shown the feasibility of this approach for azetidine synthesis. The stereochemical course of the reaction has also been delineated.[6] Okuma *et al.* have used this methodology for obtaining oxetanes.[7] In this paper, we define the scope and limitations of this procedure and delineate the mechanism of the reaction.

Results and Discussions

Except for 6, the *N*-arylsulphonylaziridines **3**–**18** were prepared by a known three-step sequence[8] (Scheme 2). The adducts **1** were obtained as oils and used as such; this presented no difficulties in subsequent steps. The last step did, however, pose problems in a few cases. Thus, the aziridines **9**, **13**, **14** and **15** were found to be contaminated when the corresponding sulphonamide was cyclised with alcoholic NaOH according to the reported method (Method A). In these cases, use of aqueous NaOH proved advantageous (Method B). Attempts to prepare 2-methyl-2-phenyl-*N*-phenylsulphonylaziridine by this



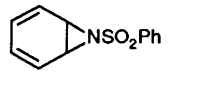
Scheme 2 *Reagents:* i, $CHCl_3$; ii, $NaHSO_3$; iii, Method A: Alc.NaOH; Method B: Aq.NaOH

procedure led instead to the aziridine **15**. The three-step sequence also failed for **6** and it was, therefore, obtained by treating propylenimine with $PhSO_2Cl$ in the presence of Et_3N (Method C).[9]

Since this aziridine synthesis led to a mixture of geometrical isomers, these were separated and characterized as reported by us previously.[6] However, only one diastereoisomer was obtained in the case of **13** and **14**.

	R^1	R^2		R^1	R^2	R^3	R^4
3	Ph	Ph	**7**	*p*-MeC_6H_4	H	H	H
4	*p*-MeC_6H_4	Ph	**8**	*m*-MeC_6H_4	H	H	H
5	*p*-ClC_6H_4	Ph	**9**	*p*-ClC_6H_4	H	H	H
6	*p*-MeC_6H_4	Me	**10**	*m*-ClC_6H_4	H	H	H
			11	*m*-$O_2NC_6H_4$	H	H	H
			12	$PhCH_2$	H	H	H
			13	Ph	H	H	Me
			14	Et	H	Me	H
			15	Ph	CH_2Cl	H	H
			16	*p*-$O_2NC_6H_4$	H	H	H

17



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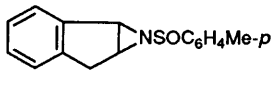


19 *p*-ClC_6H_4—CH(OEt)—CH_2NHSO_2Ph

Table 1 Preparation of *N*-arylsulphonylaziridines

Aziridine	M.p. (Lit. m.p.) (°C)	Yield[a] (%)	Method of preparation
3	74–75 (75–76)[8a]	87	**A**
4	88–89 (88–89)[8a]	97	**A**
5	97–99	97	**A**
6	60–61	65	**C**
7	63–64	55	**A**
8	Oil[b]	95	**A**
9	78–79	62	**B**
10	Oil[b]	78	**A**
11	124–125	61	**A**
12	67–68	76	**B**
13	Oil[b]	98	**B**
14	41–42	71	**B**
15	101–102	75	**B**
16	94–95	50	**A**
17	59–60 (60–61)[18]	68	**A**
18	142–144 (144–145)[8b]	90	**A**

[a] Yields are of isolated product. [b] These decomposed on distillation.

All the *N*-arylsulphonylaziridines, except **8**, **10** and **13**, which were viscous high boiling oils, were crystalline solids (Table 1). Their spectral properties and analyses were as expected (Table 2).

Reaction of the aziridines **3–14** with dimethyloxosulphonium methylide **20** (1.5 equiv.) at ambient temperature under N_2 gave the corresponding azetidines 22–33 (5–77%) (Table 3) and the sulphoxides **34** 0–30% (Scheme 3). The products were characterized on the basis of their spectral properties and elemental analyses (Table 4). The identity of the sulphoxides **34a** and **34b** was confirmed by preparing them by reaction of dimethylsulphinyl carbanion with compounds **3** and **4** respectively.

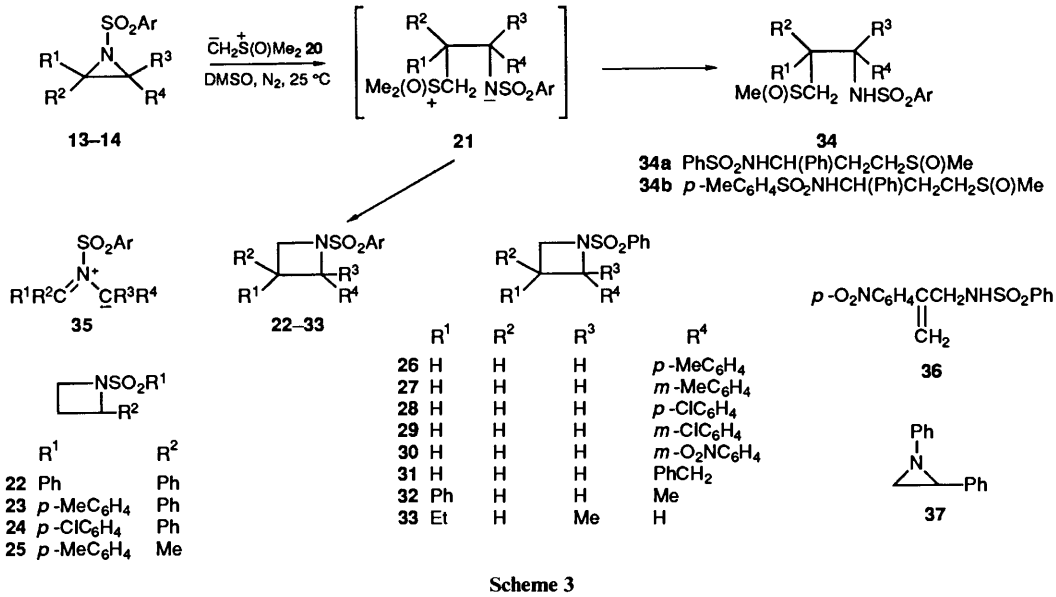
A perusal of Table 3 and examples cited in ref. 6 shows that this azetidine synthesis is quite general. It can be used to prepare 2-alkyl, 2-aryl, 2-benzyl, 2,3-dialkyl and 2,3-diaryl-*N*-arylsulphonylazetidines. Although the yields are only fair to good, they compare favourably with those generally reported for this class of compounds. Besides, the starting aziridines are relatively easy to prepare and the methylene transfer reaction is simple and convenient. Also the reaction is stereospecific and in all cases studied only one regioisomer of the azetidine is formed. Since cleavage of N–SO_2Ar bond in azetidines is known[10], the method can be used to prepare *N*-unsubstituted azetidines.

Yields of the azetidines **26–30** (Table 3) and failure to obtain the azetidine corresponding to **16**—which in fact yielded **36** (Scheme 3)—show that the reaction is greatly affected by substituents on the 2-phenyl group although no simple electronic or steric effect is discernible. The synthesis also fails for fused azetidines, none being obtained from **17** and **18** and in the case where the aziridine does not have an arylsulphonyl group on nitrogen **37** (Scheme 3).

The effect of variation of ylide nucleophilicity on the course of the reaction was also studied. The less nucleophilic 'stabilised' ylide, dimethylsulphonium ethoxycarbonylmethylide failed to react with the aziridines **3** and **4** whereas the more nucleophilic dimethylsulphonium methylide **44** gave intractable mixtures. However **44** yielded the olefins **46–49** with the disubstituted aziridines **38–43** (Scheme 4); higher conc. (4 equiv.) of the ylide and *trans* geometry of the aziridines gave higher yields of the olefins (see Experimental section).

Mechanism.—The above methodology (Scheme 3) envisages a nucleophilic attack of the ylide **20** on the aziridine ring giving the betaine **21** followed by a 1,4-elimination. In terms of this rationale the role of arylsulphonyl group is to make the aziridines electrophilic enough to be attacked by the ylide. Failure of the aziridine **37** (Scheme 3) to react with **20** bears this out. The arylsulphonyl group on nitrogen was also used to test the intermediacy of the azomethine ylide[11] **35** by making it unstable and therefore unlikely to be formed during the mild reaction conditions used. Indeed, *N*-arylsulphonylaziridines were found thermally stable so that **3** and **4** could be recovered unchanged after refluxing (8 h) in ethanol. This was further confirmed by their failure to react either neat or in dry toluene with DMAD and dimethyl fumarate.[12]

The stereospecificity of the reaction with inversion at the attacked carbon also favours this mechanism. Appreciable yields of the azetidines **25** and **33** also support non-intermediacy of **35** since electron-donating groups are known[13] to destabilize such intermediates. In terms of the above mechanism the sulphoxides **34** may be presumed to be formed through loss of a methyl group from the betaine **21** to solvent DMSO.



Scheme 3

Table 2 Selected spectral and analytical data of unknown *N*-arylsulphonylaziridines

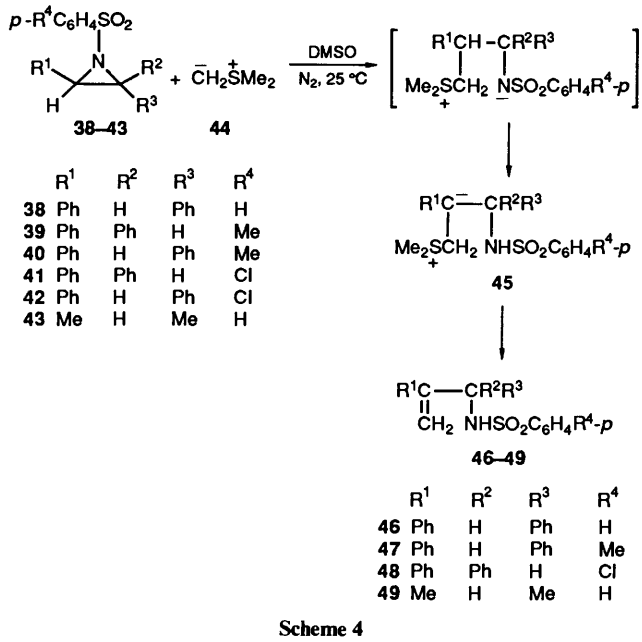
Aziridine	^{1}H NMR[a] ($CDCl_3$) (δ)	^{13}C NMR[b] ($CDCl_3$) (δ)	Anal. Found (Calc'd) C, H, N %	Molecular ion peak (M^+)
5	7.82 (2 H, d), 7.25 (7 H, m), 3.7 (1 H, dd, *J* 7 & 4), 2.95 (1 H, d, *J* 7), 2.35 (1 H, d, *J* 7)	130.24–127.07, 40.6 (d), 35.8 (t)	57.0, 3.8, 4.65 (57.24, 4.08, 4.77)	293
6	7.81–7.32 (4 H, m), 2.82 (1 H, m), 2.6 (1 H, d, *J* 7), 2.44 (3 H, s), 2.02 (1 H, d, *J* 4), 1.26 (3 H, d, *J* 6)	144.35–127.73, 35.82 (d), 34.66 (t), 21.6 (q), 16.77 (q)	56.55, 5.95, 6.8 (56.87, 6.16, 6.63)	211
7	7.08–8.2 (9 H, m), 3.76 (1 H, dd, *J* 7 & 4), 2.98 (1 H, d, *J* 8), 2.38 (1 H, d, *J* 4), 2.28 (3 H, s)	137.95–126.36, 41.0 (d), 35.73 (t), 21.0 (q)	65.85, 5.8, 5.35 (65.93, 5.49, 5.12)	273
8	8.0–6.93 (9 H, m), 3.75 (1 H, dd, *J* 8 & 4), 2.97 (1 H, d, *J* 7), 2.35 (1 H, d, *J* 4), 2.24 (3 H, s)	138.16–123.64, 41.04 (d), 35.8 (t), 21.2 (q)	65.6, 5.7, 5.0 (65.93, 5.49, 5.12)	273
9	8.0–7.82 (9 H, m), 3.77 (1 H, dd, *J* 8 & 4), 3.0 (1 H, d, *J* 7), 2.36 (1 H, d, *J* 4)	137.87–128.03, 40.04 (d), 36.22 (t)	57.55, 4.3, 4.6 (57.24, 4.08, 4.77)	293
10	8.01–7.07 (9 H, m), 3.76 (1 H, dd, *J* 8 & 4), 2.98 (1 H, d, *J* 7), 2.35 (1 H, d, *J* 4)	137.58–124.86, 40.02 (d), 36.07 (t)	57.15, 4.3, 4.55 (57.24, 4.08, 4.77)	293
11	8.19–7.27 (9 H, m), 3.9 (1 H, dd, *J* 8 & 4), 3.06 (1 H, d, *J* 7), 2.42 (1 H, d, *J* 4)	148.35–121.5, 39.68 (d), 36.51 (t)	54.9, 4.0, 9.4 (55.26, 3.95, 9.21)	304
12	7.89–7.0 (10 H, m), 3.0 (compl. mult.), 2.70 (3 H, compl. mult.), 2.17 (1 H, d, *J* 4)	137.72–126.52, 41.2 (d), 37.24 (t), 32.7 (t)	65.8, 5.1, 5.25 (65.93, 5.49, 5.12)	—
13	7.99–7.2 (10 H, m), 3.82 (1 H, d, *J* 4), 2.94 (1 H, quintet, *J* 5), 1.85 (3 H, d, *J* 6)	138.31–127.5, 46.16 (d), 41.78 (d), 11.95 (q)	65.6, 5.3, 4.85 (65.93, 5.49, 5.12)	273
14	8.0–7.43 (5 H, m), 2.9 (1 H, quintet, *J* 6), 2.72 (1 H, q, *J* 6), 1.44 (compl. mult), 1.21 (3 H, d, *J* 4), 0.83 (3 H, t, *J* 8)	138.45–127.68, 46.6 (d), 40.4 (d), 19.75 (t), 11.8 (q), 11.32 (q)	58.5, 6.45, 6.2 (58.67, 6.67, 6.22)	225
15	7.96–7.25 (10 H, m), 4.36–4.08 (2 H, AB quartet), 2.99 (1 H, s), 2.86 (1 H, s)	135.28–127.67, 54.30 (s), 47.51 (t), 59.20 (t)	58.2, 4.55, 4.15 (58.53, 4.55, 4.55)	307
16	8.21–7.26 (9 H, m), 3.88 (1 H, dd, *J* 7 & 4), 3.08 (1 H, d, *J* 7), 2.40 (1 H, d, *J* 4)	147.8–123.78, 39.76 (d), 36.6 (t)	55.2, 3.85, 9.15 (55.26, 3.95, 9.21)	304

[a] Multiplets for which *J* is not shown are complex multiplets. [b] Peaks for aromatic protons and carbons have not been indicated individually; rather the range in which they appear is shown. [c] *J* values in Hz.

Table 3 Synthesis of *N*-arylsulphonylazetidines

Azetidine	M.p. (Lit. m.p.) (°C)	Yield[a] (%)
22	124.5–125 (123.5–125)[19]	51
23	118–119.5	52
24	149–150	72
25	93–94	50
26	82–83	20
27	78–79	29
28	150–151	18
29	86–87	30
30	179–180	5
31	111–112	34
32	93–94	77
33	Oil[b]	65

[a] Yields are of isolated product. [b] These decomposed on distillation.



	R^1	R^2	R^3	R^4
38	Ph	H	Ph	H
39	Ph	Ph	H	Me
40	Ph	H	Ph	Me
41	Ph	Ph	H	Cl
42	Ph	H	Ph	Cl
43	Me	H	Me	H

	R^1	R^2	R^3	R^4
46	Ph	H	Ph	H
47	Ph	H	Ph	Me
48	Ph	Ph	H	Cl
49	Me	H	Me	H

Scheme 4

The regiochemical course of the reaction is apparently substituent dependent and governed by conflicting steric and electronic considerations. With the exception of **16**, the aziridines having an unsubstituted carbon **3–12** gave products derived from attack at the unsubstituted carbon indicating dominance of steric effects. On the other hand, reaction of the aziridines **13** and **14** with the ylide **20** leads to products derived from attack at the carbon bearing a phenyl rather than a methyl and a methyl rather than an ethyl group, indicating preponderance of electronic effects. Similar observations about substituent (and nucleophile) dependence of regiochemistry of ring opening of aziridines have been made by others.[14] In the case of the aziridine **16**, the olefin formed, **36**, apparently arises through attack on the substituted carbon followed by abstraction of the benzylic proton by the nitrogen anion in **21** and elimination of DMSO.

Formation of the olefins **46–49** (Scheme 4) rather than the azetidines upon reaction of the aziridines **38–43** with the ylide **44**, may be due to the poorer leaving group ability of dimethyl sulphide as compared to DMSO. This leads to formation of the anion **45** (similar to the one formed in reaction of aziridine **16** with the ylide **20**) and elimination to olefins. The more facile reaction of the *trans*-isomers **40** and **42** with the ylide **44** as compared to *cis*-isomers **39** and **41** has a precedent in Stamm's work.[15]

Experimental

M.p.s and b.p.s are uncorrected. IR spectra were recorded on a Nicolet 5 DX FTIR instrument. ^{1}H and ^{13}C NMR ($CDCl_3$) spectra were recorded on a JEOL FX 100 machine at 100 and 25

Table 4 Selected spectral and analytical data of unknown *N*-arylsulphonylazetidines

Azetidine	^{1}H NMR[b] ($CDCl_3$) (δ)	^{13}C NMR[b] ($CDCl_3$) (δ)	Anal. Found (Calc'd) C, H, N %	Molecular ion peak (M^+)
23	8.35–7.25 (9 H, m), 4.9 (1 H, t, *J* 8), 3.78 (2 H, t, *J* 9), 2.28 (2 H, m), 2.44 (3 H, s)	146–127.6, 66.4 (d), 48.0 (t), 26.0 (t), 22.0 (q)	66.7, 6.05, 4.65 (66.89, 5.92, 4.87)	287
24	7.83–7.17 (9 H, m), 4.94 (1 H, t, *J* 8), 3.84 (2 H, t, *J* 8), 2.3 (2 H, m)	144–127.6, 66.4 (d), 48.0 (t), 26.0 (t)	58.25, 4.85, 4.35 (58.53, 4.55, 4.55)	307
25	7.89–7.26 (4 H, m), 4.07–3.36 (3 H, m), 2.46 (3 H, s), 1.93 (2 H, m), 1.40 (3 H, d, *J* 7)	143.8–128.26, 60.28 (d), 47.46 (t), 24.07 (t), 22.27 (q), 21.54 (q)	58.4, 6.3, 6.3 (58.67, 6.67, 6.22)	225
26	7.83–7.0 (9 H, m), 4.87 (1 H, t, *J* 8), 3.77 (2 H, dd, *J* 8 & 6), 2.33 (3 H, s), 2.28 (2 H, m)	137.82–126.41, 65.85 (d), 47.38 (t), 25.98 (t), 21.26 (q)	66.6, 6.1, 4.75 (66.89, 5.92, 4.87)	287
27	7.85–7.1 (9 H, m), 4.87 (1 H, t, *J* 8), 3.79 (2 H, t, *J* 7), 2.33 (3 H, s), 2.24 (2 H, m)	140.29–123.3, 65.83 (d), 47.27 (t), 25.83 (t), 21.39 (q)	66.75, 5.75, 4.9 (66.89, 5.92, 4.87)	287
28	7.82–7.3 (9 H, m), 4.89 (1 H, t, *J* 8), 3.77 (2 H, dd, *J* 8 & 6), 2.25 (2 H, m, *J* 8)	139.14–127.83, 65.11 (d), 47.43 (t), 25.89 (t)	58.55, 4.7, 4.5 (58.53, 4.55, 4.55)	307
29	7.89–7.14 (9 H, m), 4.89 (1 H, t, *J* 7), 3.8 (2 H, dd, *J* 9 & 6), 2.24 (2 H, m, *J* 7)	142.49–124.41, 64.86 (d), 47.27 (t), 25.86 (t)	58.05, 4.7, 4.55 (58.53, 4.55, 4.55)	307
30	8.2–7.26 (9 H, m), 5.04 (1 H, t, *J* 7), 3.86 (2 H, dd, *J* 9 & 6), 2.3 (2 H, m)	133.42–121.34, 64.37 (d), 47.37 (t), 25.63 (t)	56.2, 4.35, 8.6 (56.6, 4.4, 8.8)	318
31	7.92–7.2 (10 H, m), 4.06 (1 H, m), 3.53 (2 H, m), 3.11 (2 H, m), 1.92 (2 H, m)	136.3–126, 64.18 (d), 47.56 (t), 41.96 (t), 21.69 (t)	66.65, 5.95, 5.1 (66.89, 5.92, 4.87)	—(C)
32	7.92–7.32 (10 H, m), 4.26 (1 H, quintet, *J* 7), 3.93 (2 H, d, *J* 6), 3.4 (1 H, m), 0.98 (3 H, d, *J* 7)	137.38–127.20, 63.02 (d), 53.47 (t), 38.17 (d), 17.02 (q)	66.6, 5.85, 5.1 (66.89, 5.92, 4.87)	287
33	7.89–7.46 (5 H, m), 3.82 (1 H, t, *J* 7), 3.35 (1 H, m), 3.11 (1 H, t, *J* 7), 2.2 (1 H, m, *J* 7), 1.75 (2 H, m), 0.9 (3 H, t, *J* 7), 0.81 (3 H, d, *J* 7)	135.17–128.16, 72.56 (d), 54.87 (t), 30.16 (d), 28.21 (t), 18.52 (q), 8.48 (q)	59.95, 7.15, 5.8 (60.25, 7.11, 5.85)	239

[a] Multiplets for which *J* is not shown are complex multiplets. [b] Peaks for aromatic protons and carbons have not been indicated individually; rather the range in which they appear is shown. [c] This compound did not show a molecular ion peak. [d] *J* values in Hz.

MHz respectively using TMS as internal standard. Mass spectra were obtained on JEOL G/C MS JMS D300 spectrometer. Microanalyses were carried out on Perkin-Elmer 240C CHN element analyser. Reactions were monitored by TLC using benzene–light petroleum (b.p. 40–60 °C) mixtures for developing the plates. Unless otherwise specified, anhydrous Na_2SO_4 was used as the drying agent.

General Method for Preparation of N-*Arylsulphonylaziridines.*—These compounds were obtained through the following modification of a British Patent procedure.[8a] A solution of the pertinent *N*,*N*-dichloroarylsulphonamide[16] (0.01 mol) and the olefin (0.01 mol) in $CHCl_3$ (100 cm^3) was refluxed under N_2 (5–6 h). The cooled reaction mixture was treated (2–3 h) with 20% aqueous $NaHSO_3$ (100 cm^3) at room temp. From the resultant biphasic mixture the organic layer was separated, washed with aqueous $NaHCO_3$ and water and dried. Removal of the solvent and recrystallisation from $CHCl_3$–light petroleum (b.p. 40–60 °C) (1:1) gave the pure sulphonamides **2**. Cyclisation was carried out by adding 20% aqueous NaOH (10 cm^3) to a solution of **2** in 95% EtOH and stirring (5–10 min) the mixture at room temp. when the aziridine precipitated out (Method A); alternatively, aqueous NaOH according to the procedure of Gensler[17] (Method B) was employed. Physical and spectral data for *N*-arylsulphonylaziridines are given in Tables 1 and 2.

General Method for the Synthesis of N-*Arylsulphonylazetidines.*—The pertinent aziridine (1 equiv.) dissolved in DMSO (5–10 cm^3) was added to a solution of dimethyloxosulphonium methylide **20** (1.5 equiv.) in DMSO (5–10 cm^3) and the mixture stirred (18–20 h) at ambient temperature. It was then quenched with water (150 cm^3) and extracted with ether and the extracts were washed with water and dried. Removal of the solvent and column chromatography of the residue on silica gel gave, on elution with benzene, the azetidines **22–33** which were crystallised from benzene–light petroleum (b.p. 40–60 °C). Physical and spectral data for the *N*-arylsulphonylazetidines are given in Tables 3 and 4. Further elution with benzene–ethyl acetate (10:1) gave the sulphoxides **34**. The aqueous layer was neutralized with glacial acetic acid and extracted with ethyl acetate. The extracts were washed with water, dried and evaporated to furnish additional amounts of **34**.

Reaction of 2-p-*Nitrophenyl*-N-*phenylsulphonylaziridine* **16** *with Dimethyloxosulphonium Methylide* **20**.—The ylide **20** (4.15 mmol) was treated (20 h) with the aziridine **16** (0.840 g, 2.76 mmol) as above. Work-up followed by column chromatography on silica gel gave, on elution with $CHCl_3$–light petroleum (b.p. 40–60 °C) (1:1) the olefin **36** (0.52 g, 59%), m.p. 147–148 °C [from ethyl acetate–light petroleum (b.p. 40–60 °C)] (Found: C, 56.85; H, 3.95; N, 8.9 $C_{15}H_{14}N_2SO_4$ requires C, 56.60; H, 4.40; N, 8.81%); ν_{max}/cm^{-1} 3240 (NH), 1325 and 1164 (SO_2) and 1600 (C=CH_2); δ_H(100 MHz, $CDCl_3$) 8.16–7.25 (9 H, m), 5.52 (1 H, s), 5.41 (1 H, s), 4.63 (1 H, br m) and 4.05 (2 H, d, *J* 6); δ_C 146.58–123.00 (Ar*C*), 118.36 (t) and 45.71 (t); *m*/*z* 318 (M^+).

General Method for Reaction of N-*Arylsulphonylaziridines with Dimethylsulphonium Methylide* **44**.—*N*-Arylsulphonylaziridines **38–43** (1 equiv.) in DMSO (5 cm^3) were added dropwise to a solution of the ylide **44** (4 equiv.) in DMSO–THF (1:1) (25 cm^3) under N_2 at −5 °C. The mixture was stirred at this temperature for 1 h and room temp. for 8 h. THF was removed under reduced pressure and the contents poured into ice cold water (150 cm^3). The mixture was extracted with $CHCl_3$ and the extracts were washed with water, dried, and evaporated. Column chromatography of the residue on silica gel gave, on elution with benzene, first unchanged aziridines and then the olefins **46–49**.

Reaction of trans-2,3-*Diphenyl*-N-*phenylsulphonylaziridine* **38** *with* **44**.—The *trans*-aziridine **38** (3.35 g, 10 mmol), on reaction with the ylide **44** (40 mmol) as above gave unchanged **38** (0.41 g, 12.1%) and the olefin **46**, (2.45 g 70.2%), m.p. 161–162 °C [from

ethyl acetate–light petroleum (b.p. 40–60 °C)] (Found: C, 71.95; H, 5.65; N, 3.8. $C_{21}H_{19}NSO_2$ requires C, 72.21; H, 5.49; N, 4.01%); ν_{max}/cm^{-1} 3273 (NH), 1618 (C=CH_2), 1316 and 1152 (SO_2); $\delta_H(CDCl_3)$ 7.73–7.02 (15 H, s), 5.5 (1 H, d *J* 8; collapses to a singlet on D_2O exchange), 5.35 (1 H, s), 5.15 (1 H, s), 5.0 (1 H, d *J* 7; disappears on D_2O exchange); $\delta_C(CDCl_3)$ 147.10–120.80 (Ar*C*), 111.00 (t) and 60.96 (d); *m/z* 349 (M^+).

Reaction of cis-2,3-*Diphenyl*-N-p-*tolylsulphonylaziridine* **39** *with Ylide* **44**.—The *cis*-aziridine **39** (1.047 g, 3 mmol), on reaction with the ylide **44** (12 mmol) as above, gave unchanged aziridine **39** (0.837 g, 80%) and no olefin.

Reaction of trans-2,3-*Diphenyl*-N-p-*tolylsulphonylaziridine* **40** *with the Ylide* **44**.—The *trans*-aziridine **40** (3.49 g, 10 mmol), on reaction with the ylide **44** (40 mmol) as above, gave the unchanged aziridine (1.029 g, 29.5%) and the olefin **47** (1.367 g, 37.7%), m.p. 120–121 °C [from ethyl acetate–light petroleum (b.p. 40–60 °C)] (Found: C, 72.5; H, 5.95; N, 4.15. $C_{22}H_{21}NSO_2$ requires C, 72.72; H, 5.79; N, 3.86%) ν_{max}/cm^{-1} 3261 (NH), 1603 (C=CH_2), 1322 and 1164 (SO_2); $\delta_H(CDCl_3)$ 7.62–7.10 (14 H, m), 5.46 (1 H, d *J* 7; collapses to a singlet on D_2O exchange), 5.37 (1 H, s), 5.16 (1 H, s), 5.1 (1 H, d disappears on D_2O exchange) and 2.38 (3 H, s); $\delta_C(CDCl_3)$ 147.37–127.54 (Ar*C*), 116.53 (t), 61.07 (d) and 21.65 (q); *m/z* 363 (M^+).

Reaction of cis-2,3-*Diphenyl*-N-p-*chlorophenylsulphonylaziridine* **41** *with* **44**.—The *cis*-aziridine **41** (1.25 g, 3.4 mmol), on reaction with the ylide **44** (13 mmol) as above, gave the unchanged aziridine (0.876 g, 70%) and the olefin **48** (0.066 g, 5%), m.p. 138–139 °C [from ethyl acetate– light petroleum (b.p. 40–60 °C)] (Found: C, 65.35; H, 4.8; N, 3.6. $C_{21}H_{18}ClNSO_2$ requires C, 65.79; H, 4.69, N, 3.65%), ν_{max}/cm^{-1} 3261 (NH), 1600 (C=CH_2), 1328 and 1164 (SO_2); $\delta_H(CDCl_3)$ 7.62–7.10 (14 H, m), 5.5 (1 H, d, *J* 7; collapses to a singlet on D_2O exchange), 5.4 (1 H, s), 5.13 (1 H, d, disapppears on D_2O exchange), 5.1 (1 H, s); $\delta_C(CDCl_3)$ 147.2–126.71 (Ar*C*) 116.77 (t) and 61.07 (d); *m/z* 383 (M^+).

Reaction of trans-2,3-*Diphenyl*-N-p-*chlorophenylsulphonylaziridine* **42** *with* **44**.—The *trans*-aziridine **42** (1.88 g, 5.1 mmol) on reaction with the ylide **44** (20 mmol) as above gave the olefin **48** (1.34 g, 68.7%).

Reaction of trans-2,3-*Dimethyl*-N-*phenylsulphonylaziridine* **43** *with* **44**.—The *trans*-aziridine **43** (1 g, 4.7 mmol), on reaction with the ylide **44** (17 mmol) as above, gave unchanged aziridine (0.678 g, 67.8%) and the olefin **49** (0.168 g, 15.7%) as an oil (Found: C, 58.5; H, 6.6; N, 6.2. $C_{11}H_{15}NSO_2$ requires C, 58.66; H, 6.66; N, 6.22%); ν_{max}/cm^{-1} 3291 (NH), 1609 (C=CH_2) and 1328 and 1164 (SO_2); $\delta_H(CDCl_3)$ 7.99–7.40 (5 H, m), 4.91 (1 H, d *J* 8), 4.79 (1 H, s), 3.86 (1 H, quintet, *J* 7; collapses to a quartet on D_2O exchange), 1.55 (3 H, s) and 1.17 (3 H, d, *J* 7); $\delta_C(CDCl_3)$ 144.80–127.00 (Ar*C*), 111.98 (t), 54.82 (d) and 20.61 (q); *m/z* 225 (M^+).

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