Reaction of *N*-arylsulfonylaziridines with dimethylsulfonium-ethoxycarbonyl methylide: regio- and stereo-selective synthesis of 1-arylsulfonyl-2-ethoxycarbonyl azetidines

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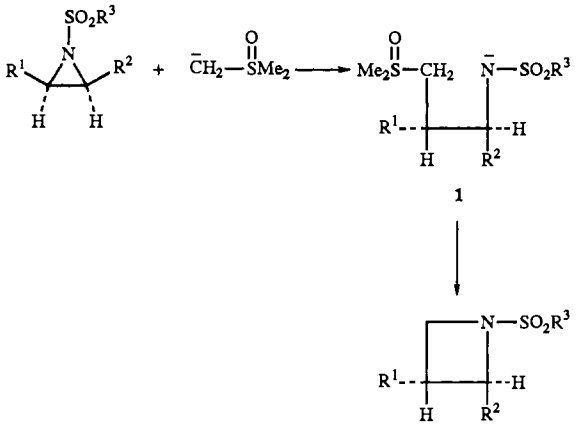
Synthesis and characterization of 4-aryl-, 3,4-diaryl- and 3-alkyl-4-aryl-*N*-arylsulfonylazetidines, bearing a 2-ethoxycarbonyl group are described. The methodology used involves transfer of an ethoxycarbonyl substituted methylene group from dimethylsulfoniumethoxycarbonyl methylide to *N*-arylsulfonylaziridines. The synthesis is both regio- and stereo-selective.

Azetidines are an important group of nitrogen heterocycles for which few general syntheses are known.[1-3] Previously we have shown[4-6] that methylene transfer from dimethylsulfoxonium methylide to *N*-arylsulfonylaziridines leads, in a fairly simple and general way, to nucleophilic attack of the ylide on the aziridine to give an intermediate **1** which undergoes a 4-*exo*-*tet* ring closure to the corresponding azetidine (Scheme 1). To



Scheme 1

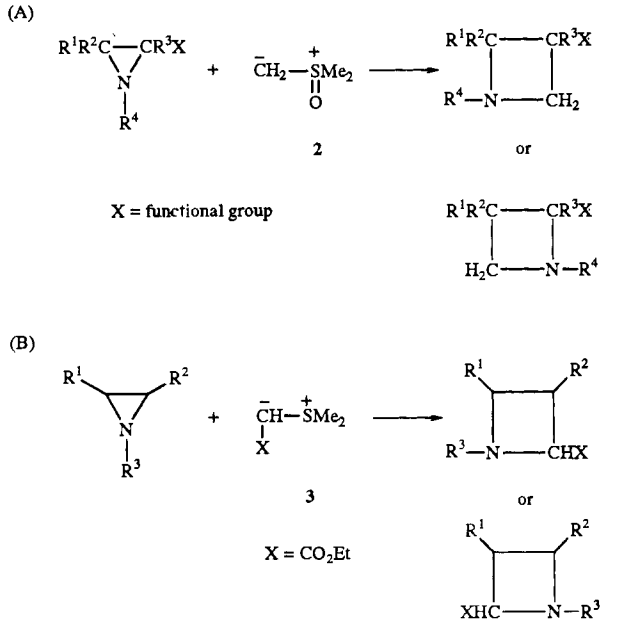
investigate the versatility of this approach it was considered desirable to explore the possibility of preparing functionalized azetidines through this procedure. We now report the results of efforts in this direction.

Results and discussion

Based on the rationale of a synthesis which we developed (Scheme 1), two approaches (A and B) could be envisaged to extend the synthesis to functionalized azetidines. These are outlined in Scheme 2.

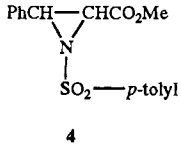
In (A), an aziridine carrying a functionality such as an ester group, which can be transformed relatively easily to other functional groups and does not itself react readily with the ylide,[7] could be treated with dimethylsulfoxonium methylide **2** to yield the corresponding azetidine. On the other hand approach (B) would involve reaction of the appropriate aziridine with a ylide such as **3**, carrying an ester functionality on the ylide carbon, which is known to transfer[8-11] substituted methylene to suitable substrates.

Approach (A) was studied through preparation of the aziridine **4** by a literature procedure[12] and allowing it to react



Scheme 2

with dimethylsulfoxonium methylide under different reaction conditions. However, in each case a complex mixture was obtained from which no pure product could be isolated, even after careful chromatography. This, together with the fact that aziridines like **4** are relatively difficult to prepare,[13] led us to focus our attention on approach (B).



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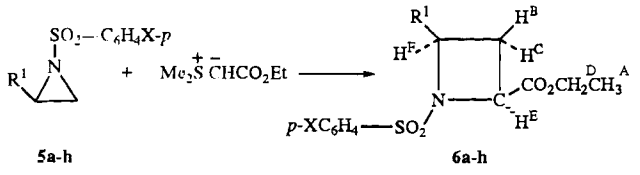
Aziridines **5a–h** were prepared, according to our previously reported procedure[6] and treated with dimethyl sulfoniumethoxycarbonyl methylide **3** in dry DMF at 50 °C for 2–3 h followed by stirring at room temperature for 18 h. Work-up, followed by column chromatography, led to the corresponding azetidines **6a–h** in 5–44% isolated yields (Table 1) (Scheme 3).

The azetidine structures were assigned on the basis of spectral

Table 1 Reaction of 2-substituted-*N*-arylsulfonylaziridines with dimethylsulfoniumethoxycarbonyl methylide

Azetidine	δ_H	δ_C	Yield (%)
6a	1.27 (t, *J* 7, 3 H, $CO_2CH_2CH_3$) 2.29 (m, 1 H, CH_2), 2.82 (m, 1 H, CH_2), 4.22 (q, *J* 7, 2 H, $CO_2CH_2CH_3$), 4.78 (t, *J* 8, 1 H, $CHCO_2C_2H_5$), 5.17 (t, *J* 8, 1 H, PhC*H*), 7.10–7.96 (m, 10 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 29.4 (t, CH_2), 56.9 (t, $CO_2CH_2CH_3$) 61.5 (d, $CHCO_2C_2H_5$), 62.4 (d, PhCH), 126.7, 129.7, 130.4, 130.8, 131.2, 135.2, 139.3 (Ar*C*) and 176.0 (s, C=O).	41
6b	1.25 (t, *J* 7, 3 H, $CO_2CH_2CH_3$), 2.38 (s, 3 H, SO_2PhCH_3), 2.60 –2.89 (m, 2 H, CH_2), 4.22 (q, *J* 7, 2 H, $CO_2CH_2CH_3$), 4.64 (t, *J* 8.1, 1 H, $CHCO_2C_2H_5$) 5.06 (t, *J* 8.1, 1 H, PhC*H*), 7.05–7.78 (m, 9 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 21.5 (q, PhCH_3), 29.6 (t, CH_2), 56.9 (t, $CO_2CH_2CH_3$), 61.4 (d, $CHCO_2C_2H_5$), 62.3 (d, PhCH), 126.7, 127.4, 128.2, 128.6, 129.1 and 129.3 (Ar*C*).	34
6c	1.25 (t, *J* 7, 3 H, $CO_2CH_2CH_3$), 2.30 (m, 1 H, CH_2), 2.81 (m, 1 H, CH_2), 4.23 (q, *J* 7, 2 H, $CO_2CH_2CH_3$), 4.78 (dd, J_1 8, J_2 9, 1 H, $CHCO_2C_2H_5$), 5.17 (t, *J* 8, 1 H, PhC*H*) and 7.25–7.96 (m, 9 H, Ar*H*).	14.0 (q, $CO_2CH_2CH_3$), 29.4 (t, CH_2), 56.9 (t, $CO_2CH_2CH_3$), 61.5 (d, $CHCO_2C_2H_5$), 62.4 (d, PhCH), 126.7, 127.5, 127.8, 128.4, 128.8, 129.5, 137 (ArC) and 169.9 (C=O).	43
6d	1.24 (t, *J* 7, 3 H, $CO_2CH_2CH_3$), 2.25 (m, 1 H, CH_2), 2.81 (m, 1 H, CH_2), 4.22 (q, *J* 7, 2 H, $CO_2CH_2CH_3$), 4.69 (t, 1 H, *J* 8.3, $CHCO_2C_2H_5$), 5.16 (t, 1 H, *J* 8.3, PhC*H*) and 7.18–7.82 (m, 9 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 29.4 (t, CH_2), 56.9 (t, $COOCH_2CH_3$), 61.5 (d, $CHCO_2C_2H_5$), 62.3 (d, PhC*H*), 128, 128.4, 128.5, 129.8 and 133.1 (ArC).	39
6e	1.23 (t, *J* 7.2, 3 H, $CO_2CH_2CH_3$), 2.24 (m, 1 H, CH_2), 2.80 (m, 1 H, CH_2), 4.21 (q, *J* 7.2, 2 H, $CO_2CH_2CH_3$), 4.71 (dd, J_1 7.9, J_2 8.9, 1 H, $CHCO_2C_2H_5$), 5.09 (t, *J* 8.1 H, PhC*H*), 7.20–7.8 (m, 9 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 29.4 (t, CH_2), 56.9 (t, $CHCO_2C_2H_5$), 62.6 (d, PhC*H*), 126.8, 127.9, 128.4, 128.7, 129.2, 129.7, 133.1 and 134.4 (ArC).	43
6f	1.23 (t, *J* 7, 3 H, $CO_2CH_2CH_3$), 2.24 (m, 1 H, CH_2), 2.33 (s, 3 H, PhCH_3), 2.80 (m, 1 H, CH_2), 4.22 (q, *J* 7, 2 H, $CO_2CH_2CH_3$), 4.70 (t, *J* 8, 1 H, $CHCO_2C_2H_5$), 5.09 (t, *J* 8, 1 H, PhC*H*), 7.21–7.89 (m, 9 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 21.2 (q, PhCH_3), 29.4 (t, CH_2), 56.8 (t, $CO_2CH_2CH_3$), 61.5 (d, $CHCO_2C_2H_5$), 62.4 (d, PhC*H*), 127.1, 127.8, 128.2, 129.1, 130.1, 138.8 (ArC).	36
6g	1.26 (t, *J* 7.2, 3 H, $CO_2CH_2CH_3$), 2.28 (m, 1 H, CH_2), 2.84 (m, 1 H, CH_2), 4.24 (q, *J* 7.2, 2 H, $CO_2CH_2CH_3$), 4.73 (dd, J_1 8.05 and J_2 9.03, 1 H, $CHCO_2C_2H_5$), 5.22 (t, *J* 8, 1 H, PhC*H*) and 7.26–8.24 (m, 9 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 29.4 (t, CH_2), 56.9 (t, $CO_2CH_2CH_3$), 61.5 (d, $CHCO_2C_2H_5$), 62.4 (d, PhC*H*), 121.2, 124.4, 126.6, 126.8, 128.1, 129.2, (ArC) and 169.7 (C=O).	24
6h	1.15 (d, *J* 2.0, 3 H, CH_3CH), 1.25 (t, *J* 3.5, 3 H, $CO_2CH_2CH_3$) 2.102 (m, 2 H, CH_2), 2.41 (s, 3 H, SO_2PhCH_3), 3.92 (m, 3 H, $CO_2CH_2CH_3$ and PhC*H*), 4.08 (dd, 1 H, CH_3CH) and 7.25–7.77 (m, 4 H, ArH).	*	5

* Not enough material to characterize it.

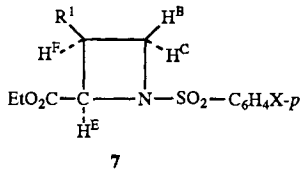


5a-h **6a-h**

a R^1 = Ph, X = H
b R^1 = Ph, X = Me
c R^1 = Ph, X = Cl
d R^1 = C_6H_4Cl-*p*, X = H
e R^1 = C_6H_4Cl-*m*, X = H
f R^1 = C_6H_4Me-*p*, X = H
g R^1 = $C_6H_4NO_2$-*m*, X = H
h R^1 = Me, X = Me

Scheme 3

data and elemental analysis. The regio-structure was decided in favour of **6**, as against **7**, on the basis of ^{1}H NMR evidence. For **7**, H^E is expected to appear as a doublet and H^B and H^C as



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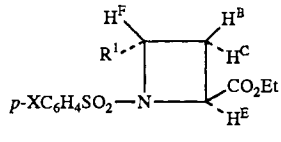
triplets or doublet of doublets, whereas in **6a–g**, H^E appears as a triplet (*J* 8 Hz) or a doublet of doublets (J_1 8 Hz, J_2 9 Hz), H^F appears as triplet (*J* 8 Hz) and H^B and H^C as multiplets. The *cis* relationship of R and the ester group was derived from the following observations. (a) Refluxing **6c** with sodium ethoxide in ethanol for 24 h led to no epimerization. This is in accord with the reported[14] observation that the *cis*-isomers of such azetidines are more stable than the *trans*-isomers and so do not epimerize readily. (b) In case of the *cis*-isomers the difference in the chemical shift of H^B and H^C would be expected to be more than in the *trans* isomer **8**. In the case of **6**, chemical-shift



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differences of 0.51–0.56 ppm were observed, which are close to 0.55 ppm reported[15] for the *cis*-isomer of methyl 1,4-diphenylazetidine-3-carboxylate; for the *trans*-isomer the value reported is 0.28 ppm. Also the chemical-shift difference between H^E and H^F is expected to be more for the *trans* than for the *cis* isomer. We observed a chemical-shift difference of 0.47 ppm which is close to 0.37 ppm reported for the *cis* isomer of methyl 1,4-diphenylazetidine-3-carboxylate; for the *trans* isomer the corresponding value is 1.22 ppm.

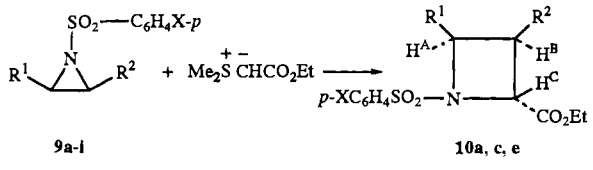
Formation of the regioisomer **6** indicates that the ylide carbon attacks the unsubstituted carbon of the aziridines in preference to the substituted carbon. This is in accord with our previous observations.[6] Alternatively, it could also mean that the intermediate derived from attack at the unsubstituted carbon goes to the product azetidine whereas that from attack at the substituted carbon prefers other competing reactions. A distinction between the two cannot be made because, except azetidine, no other pure product could be isolated and characterized. The stereochemical course of the reaction

Table 2 Reaction of 2,3-disubstituted-*N*-arylsulfonylaziridines with dimethylsulfoniumethoxycarbonyl methylide

Aziridine	Azetidine	δ_H	δ_C	Yield (%)
9a	**10a**	1.32 (t, *J* 7.1, $CO_2CH_2CH_3$), 4.21 (m, 3 H, $CO_2CH_2CH_3$, PhC*H*), 5.04 (d, *J* 4, 1 H, $CHCO_2C_2H_5$), 5.86 (d, *J* 8, 1 H, PhC*H*NSO$_2$Ph) and 6.8–7.52 (m, 15 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 44.7 (d, PhCH), 61.8 (t, $CO_2CH_2CH_3$), 66.2 (d, $CHCO_2C_2H_5$), 70.4 (d, PhCHNSO$_2$Ph), 127.0, 127.6, 127.9, 128, 128.8, 134.8 (ArC) and 170.4 (C=O).	46
9b	**10a**	1.32 (t, *J* 7.1, $CO_2CH_2CH_3$), 4.21 (m, 3 H, $CO_2CH_2CH_3$, PhC*H*), 5.04 (d, *J* 4, 1 H, $CHCO_2C_2H_5$), 5.86 (d, *J* 8, 1 H, PhC*H*NSO$_2$Ph) and 6.8–7.52 (m, 15 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 44.7 (d, PhCH), 61.8 (t, $CO_2CH_2CH_3$), 66.2 (d, $CHCO_2C_2H_5$), 70.4 (d, PhCHNSO$_2$Ph), 127.0, 127.6, 127.9, 128, 128.8, 134.8 (ArC) and 170.4 (C=O).	21
9c	**10c**	1.34 (t, *J* 7.1, 3 H, $CO_2CH_2CH_3$), 2.33 (s, 3 H, PhCH_3), 4.21 (m, 3 H, $CO_2CH_2CH_3$ and PhC*H*), 5.09 (d, *J* 4, 1 H, $CHCO_2C_2H_5$), 5.86 (d, *J* 8, 1 H, PhC*H*NSO$_2$Ar) and 6.8–7.52 (m, 15 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 21.5 (q, PhCH_3), 44.6 (d, PhC*H*), 61.8 (t, $CO_2CH_2CH_3$), 66.27 (d, $CHCO_2C_2H_5$), 70.21 (d, PhCHNSO$_2$Ar), 127.1, 127.4, 128, 128.1, 128.3, 128.9 and 129.1 (ArC)	41
9d	**10c**	1.34 (t, *J* 7.1, 3 H, $CO_2CH_2CH_3$), 2.33 (s, 3 H, PhCH_3), 4.21 (m, 3 H, $CO_2CH_2CH_3$ and PhC*H*), 5.09 (d, *J* 4, 1 H, $CHCO_2C_2H_5$), 5.86 (d, *J* 8, 1 H, PhC*H*NSO$_2$Ar) and 6.8–7.52 (m, 15 H, ArH).	14.0 (q, $CO_2CH_2CH_3$), 21.5 (q, PhCH_3), 44.6 (d, PhC*H*), 61.8 (t, $CO_2CH_2CH_3$), 66.27 (d, $CHCO_2C_2H_5$), 70.21 (d, PhCHNSO$_2$Ar), 127.1, 127.4, 128, 128.1, 128.3, 128.9 and 129.1 (ArC)	10
9e	**10e**	1.07 (d, *J* 8.4, 3 H, CH_3CH), 1.20 (t, *J* 7.1, 3 H, $CO_2CH_2CH_3$), 3.85 (dd, J_1 8.37, J_2 5.83, 1 H, PhC*H*), 4.15 (q, *J* 7.1, 2 H, $CO_2CH_2CH_3$), 4.91 (m, 1 H, CH_3CH), 4.96 (d, *J* 5.83, 1 H, $CHCO_2C_2H_5$) and 7.19–7.92 (m, 10 H, ArH).	13.8 (q, CH_3CH), 16.2 (q, $CO_2CH_2CH_3$), 42.7 (d, PhC*H*), 61.4 (t, $CO_2CH_2CH_3$), 63.9 (d, CH_3CH), 65.5 (d, $CHCO_2C_2H_5$), 127, 127.8, 128.2, 128.5, 128.7, 130.6, 134.6, 141 (ArC) and 169.6 (C=O).	43
9f	—	—	—	—
9g	—	—	—	—
9h	—	—	—	—
9i	—	—	—	—

leading to the formation of the *cis* isomer is probably a consequence of the reported greater stability of the *cis* isomer in relation to the *trans* isomer for related azetidines. Entries 4–7 (Table 1) indicate no significant electronic effect of substituents residing on the 2-phenyl ring of the aziridines on the course of the reaction, since aziridines bearing electron donating or electron withdrawing groups at *meta* or *para* positions lead to azetidines with similar yields. The small variations may be due to the ease of isolation of the products rather than any substituent electronic effects.

The synthesis could also be extended to prepare 3,4-disubstituted azetidines bearing an ethoxycarbonyl functionality at C-2 (Table 2) (Scheme 4).

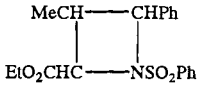


9a-i **10a, c, e**

a $R^1 = R^2 = Ph$ (*trans*), X = H
b $R^1 = R^2 = Ph$ (*cis*), X = H
c $R^1 = R^2 = Ph$ (*trans*), X = Me
d $R^1 = R^2 = Ph$ (*cis*), X = Me
e $R^1 = Ph$, $R^2 = Me$ (*trans*), X = H
f $R^1 = R^2 = Me$ (*trans*), X = H
g $R^1 = R^2 = Me$ (*cis*), X = H
h $R^1 = R^2 = Me$ (*trans*), X = Me
i $R^1 = R^2 = Me$ (*cis*), X = Me

Scheme 4

The geometric relationship of the substituents in azetidines **10** was derived from ^{1}H NMR evidence. Thus J_{AB} = 8 Hz suggests that these protons are *cis* disposed, whereas J_{BC} = 4 Hz suggests a *trans*-relationship for H_B and H_C. The larger value of J_{cis}, as compared with J_{trans}, is normal for four-membered rings[16] and has been previously observed by us for related azetidines. In the case of *trans* substrates the relative geometry of the aziridine and the azetidine seem to suggest that the aziridine carbon suffering the ylide attack undergoes an inversion of configuration. This may be explained in terms of an S_N2 attack on the aziridine ring leading to an overall inversion at the attacked carbon. For **10e**, the ^{1}H NMR data clearly disfavours the alternate regioisomeric structure **11**. This



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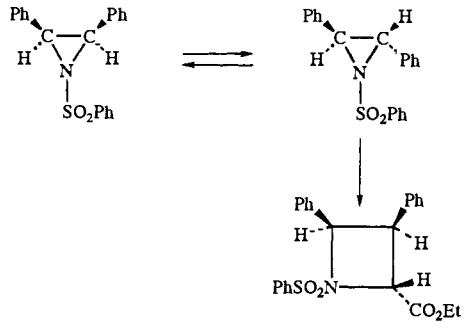
indicates that the aziridine **9e** is attacked by the ylidic carbanion at the carbon bearing the phenyl group rather than the one having a methyl group. Such discrimination has been observed by us previously for reaction of the same aziridine with dimethylsulfoxonium methylide.[6] The stereochemical assignment was again based on the relevant coupling constant values.

Interestingly, when the *cis*-isomers **9b,d** were subjected to the same reaction conditions, diminished yields of the same azetidines, as from *trans*-aziridines (**10a** and **10c**) (Table 2), were obtained and substantial amounts of the *cis*-aziridines (60 and 72%, respectively) were recovered unchanged. This, together with the fact that the recovered aziridines from the reaction of the corresponding *trans*-aziridines were found to be the *cis*-isomers, suggests that during the course of the reaction an equilibrium is set up between the *cis*- and *trans*-aziridines. Of these, only the *trans* isomers react to form the azetidine while the *cis* isomers remain unchanged (Scheme 5). The lower reactivity of the *cis* isomers, as compared to *trans* isomers, towards nucleophilic attack is well documented.[17,18] A similar observation was made in the reaction of dimethylsulfonium methylide with *cis*-2,3-diphenyl-*N*-arylsulfonylaziridines.[6] Stamm *et al.*[17] have also made similar observations for the reaction of aziridines with thiophenolate ion.



Scheme 5

The low yields of the azetidines from 2-methylaziridine (entry 8, Table 1) and the complete non-reactivity of *cis* and *trans*-2,3-dimethylaziridines (entries 6–9, Table 2) suggest that the presence of an alkyl substituent on the ring deactivates it towards nucleophilic ring opening. A further contributing factor could be the lower nucleophilicity of **3** as compared to dimethylsulfonium and dimethylsulfoxonium methylides.[19] An attempt to carry out the reaction of aziridines **5a–c** with the ylide $Me_2S^+ C^-HCOPh$ also failed possibly for similar reasons.

Conclusions

Reaction of *N*-arylsulfonylaziridines with dimethylsulfonium-ethoxycarbonyl methylide is a fairly general approach for the synthesis of azetidines bearing an ethoxycarbonyl functionality. The reaction is stereoselective and leads to the formation of only one stereoisomer. The yields are moderate but compare favourably with those reported in literature for similar compounds. However, the reaction fails completely with 2,3-dialkylaziridines and gives poor results with 2-alkyl-aziridines.

Experimental

Mps and bps are uncorrected. IR spectra were recorded on a Nicolet 5DX FTIR instrument. ^1H and $^{13}CNMR$ ($CDCl_3$) spectra were recorded on a JEOL FX100 machine at 100 and 25 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 elemental analyser. Reactions were monitored by TLC using benzene–ethyl acetate (9:1) for developing the plates. Unless otherwise specified, anhydrous Na_2SO_4 was used as the drying agent.

Ethoxycarbonylmethyldimethylsulfonium bromide

This compound was prepared according to the method of Payne,[8] in 90% yield, mp 78–81 °C (lit.,[8] mp 85–87 °C).

Dimethylsulfoniumethoxycarbonyl methylide 3

This compound was prepared according to the method of Payne[8] in 90% yield and obtained as a non-distillable viscous oil.

General method for the reaction of *N*-arylsulfonylaziridines with dimethylsulfoniumethoxycarbonyl methylide

The methylide **3** (6 mmol) was allowed to react with the appropriate *N*-arylsulfonylaziridine (2 mmol) in dry DMF (25 cm^3) under N_2 at 50 °C for 2–3 h after which it was stirred overnight at room temperature. Upon completion of the reaction, DMF was removed under reduced pressure from the mixture, after which the residue was diluted with ice-cold water (30 cm^3) and extracted with ether (3 × 25 cm^3). The combined extracts were washed with water, dried (Na_2SO_4) and evaporated and the crude product was purified by column chromatography.

***cis*-Ethyl 4-phenyl-1-phenylsulfonylazetidine-2-carboxylate 6a.** The aziridine **5a** (0.750 g, 2.89 mmol), on reaction with the ylide **3** (1.283 g, 8.67 mmol) as above, gave the azetidine **6a** (0.405 g, 40.6%), mp 105–107 °C (Found: C, 62.4; H 5.39; N, 4.35. $C_{18}H_{19}NSO_4$ requires C, 62.6; H, 5.3; N, 4.05%); ν_{max}(KBr)/cm^{-1} 2918, 1752, 1330 and 1164; *m/z* 345 (M^+).

***cis*-Ethyl 4-phenyl-1-(*p*-tolylsulfonyl)azetidine-2-carboxylate 6b.** The aziridine **5b** (0.770 g, 2.82 mmol), on reaction with the ylide **3** (1.2523 g, 8.6 mmol) as above, gave the azetidine **6b** (0.349 g, 34.3%); mp 85–87 °C (Found: C, 63.7; H, 5.9; N, 3.8. $C_{19}H_{21}NSO_4$ requires C, 63.50; H, 5.84; N, 3.89%); ν_{max}(KBr)/cm^{-1} 2910, 1752, 1330 and 1160; *m/z* 359 (M^+).

***cis*-Ethyl 1-(*p*-chlorophenylsulfonyl)-4-phenyl-azetidine-2-carboxylate 6c.** The aziridine **5c** (0.587 g, 2 mmol), on reaction with the ylide **3** (0.888 g, 6 mmol) as above, gave the azetidine **6c** (0.327 g, 43%); mp 92–93 °C (Found: C, 56.85; H, 4.65; N, 3.74. $C_{18}H_{18}ClNSO_4$ requires C, 56.91; H, 4.74; N, 3.68%); ν_{max}(KBr)/cm ^{1} 2915, 1750, 1330 and 1164; *m/z* 306 ($M^+ - CO_2Et$).

***cis*-Ethyl 4-(*p*-chlorophenyl)-1-phenylsulfonylazetidine-2-carboxylate 6d.** The aziridine **5d** (0.750 g, 2.56 mmol), on reaction with the ylide **3** (0.947 g, 6.4 mmol) as above, gave the azetidine **6d** (0.376 g, 38.8%); mp 103–105 °C (Found: C, 56.9; H, 4.8; N, 3.7. $C_{18}H_{18}ClNSO_4$ requires C, 56.91; H, 4.74; N, 3.68%); ν_{max}(KBr)/cm^{-1} 2910, 1751.6, 1330 and 1160; *m/z* 306 ($M^+ - CO_2Et$).

***cis*-Ethyl 4-(*m*-chlorophenyl)-1-phenylsulfonylazetidine-2-carboxylate 6e.** The aziridine **5e** (0.750 g, 2.56 mmol), on reaction with the ylide **3** (0.947 g, 6.4 mmol) as above, gave the azetidine **6e** (0.413 g, 42.6%), mp 77–78 °C (Found: C, 56.85; H, 4.7; N, 3.7. $C_{18}H_{18}ClNSO_4$ requires C, 56.91; H, 4.74; N, 3.68%); ν_{max}(KBr)/cm^{-1} 2905, 1752, 1334 and 1160; *m/z* 306 ($M^+ - CO_2Et$).

***cis*-Ethyl 1-phenylsulfonyl-4-(*p*-tolyl)azetidine-2-carboxylate 6f.** The aziridine **5f** (0.546 g, 2 mmol), on reaction with the ylide **3** (0.888 g, 6 mmol) as above, gave the azetidine **6f** (0.255 g, 35.4%) as an oil (Found: C, 63.6; H, 5.8; N, 3.9. $C_{19}H_{21}NSO_4$ requires C, 63.5; H, 5.84; N, 3.89%); ν_{max}/cm^{-1} 2910, 1752, 1330 and 1164; *m/z* 286 ($M^+ - CO_2Et$).

***cis*-Ethyl 4-(*m*-nitrophenyl)-1-phenylsulfonylazetidine-2-carboxylate 6g.** The aziridine **5g** (0.608 g, 2 mmol), on reaction with the ylide **3** (0.888 g, 6 mmol) as above, gave the azetidine **6g** (0.184 g, 23.6%), mp 108–110 °C (Found: C, 55.3; H, 4.7; N, 7.2. $C_{18}H_{18}N_2SO_6$ requires C, 55.38; H. 4.61; N, 7.17%); ν_{max}(KBr)/cm^{-1} 2910, 1751, 1330 and 1164; *m/z* 317 ($M^+ - CO_2Et$).

Ethyl 4-methyl-1-(*p*-tolylsulfonyl)azetidine-2-carboxylate 6h. The aziridine **5h** (0.633 g, 3 mmol), on reaction with the ylide **3** (1.332 g, 9 mmol) as above, gave the azetidine **6h** (4.4 g, 5%) as a thick oil; ν_{max}/cm^{-1} 2900, 1752, 1330 and 1164. Elution with benzene gave unchanged aziridine **5h** (60%).

Ethyl *t*-3,*t*-4-diphenyl-1-phenylsulfonylazetidine-*r*-2-carboxylate 10a. The aziridine **9a** (0.600 g, 1.79 mmol), on reaction with the ylide **3** (0.795 g, 5.37 mmol) as above, gave the azetidine **10a** (0.343 g, 45.6%); mp 112–114 °C (Found: C, 68.5; H, 5.4; N, 3.3. $C_{24}H_{23}NSO_4$ requires C, 68.41; H, 5.46; N, 3.32%); ν_{max}(KBr)/cm^{-1} 2900, 1751, 1330 and 1160; *m/z* 290 ($M^+ - SO_2Ph$).

The aziridine **9b** (0.600 g, 1.79 mmol), on reaction with the ylide **3** (0.795 g, 5.37 mmol) as above, gave the azetidine **10a** (0.155 g, 20.6%); mp 112–114 °C. Elution with benzene–hexane (8:2) gave unchanged aziridine **9b** (0.339 g, 56.6%).

Ethyl-*t*-3,*t*-4-diphenyl-1-(*p*-tolylsulfonyl)azetidine-*r*-2-carboxylate 10c. The aziridine **9c** (0.760 g, 2.17 mmol), on reaction with the ylide **3** (0.966 g, 6.53 mmol) as above, gave the

azetidine **10c** (0.381 g, 40.3%); mp 78–80 °C (Found: C, 68.16; H, 5.68; N, 3.32. $C_{25}H_{25}NSO_4$ requires C, 68.9; H, 5.74; N, 3.21%); ν_{max}(KBr)/cm^{-1} 2910, 1752, 1330 and 1164; *m/z* 280 ($M^+ - SO_2Ph - CH_3$).

The aziridine **9d** (0.380 g, 1.08 mmol), on reaction with the ylide **3** (0.483 g, 3.26 mmol) as above, gave the azetidine **10c** (0.094 g, 10%); mp 78–80 °C. Elution with benzene gave the unchanged aziridine **9d** (0.274 g, 72%).

Ethyl *t*-4-methyl,*t*-3-phenyl-1-phenylsulfonylazetidine-*r*-2-carboxylate 10e. The aziridine **9e** (0.700 g, 2.55 mmol) on reaction with the ylide **3** (1.134 g, 7.6 mmol) as above, gave the azetidine **10e** (0.393 g, 42.7%); mp 65 °C (Found: C, 63.2; H, 5.8; N, 3.9. $C_{19}H_{21}NSO_4$ requires C, 63.5; H, 5.84; N, 3.89%); ν_{max}(KBr)/cm^{-1} 2918, 1751, 1331 and 1164; *m/z* 218 ($M^+ - SO_2Ph$).

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