# Asymmetric Aziridination by Reaction of Chiral N-Sulfinylimines with Sulfur Ylides: Stereoselectivity Improvement by Use of *tert*-Butylsulfinyl Group as Chiral Auxiliary.

José L. García Ruano,*[a] Inmaculada Fernández,*[b] Miriam del Prado Catalina[a] and Ana Alcudia Cruz.[b]

[a] Departamento de Química Orgánica, Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain.
[b] Dpto. de Química Orgánica y Farmacéutica, Fac. de Farmacia, Universidad de Sevilla, 41017 Sevilla, Spain

**Abstract**: Chiral *tert*-butylsulfinyl group has been shown to be the chiral auxiliary of choice for the asymmetric aziridination of N-sulfinyliminas. Moreover, the sense of the asymmetric induction can be tuned in two ways: the chirality at the *tert*-butylsulfinyl Sulfur, or the nature of the methylene transfer reagent used. Thus, both aziridines $10(S_S,S)$ and $10(R_S,R)$, epimeric at C-2, were obtained in enantiomerically pure form by a single crystallisation (75% yield).
Copyright © 1996 Elsevier Science Ltd

## INTRODUCTION

The versatility and high reactivity of the aziridines make them very attractive starting material for the synthesis of various types of organic molecules, such as alkaloids, aminoacids and β-lactamic antibiotics.[1] Moreover, Tanner has demonstrated their utility as chiral auxiliaries and chiral ligands in efficient asymmetric synthesis.[1,2] Despite this interest, the methods for the synthesis of these compounds in enantiomerically pure form are rather limited,[1] being from optically active epoxides (obtained by asymmetric hydroxylation of alkenes or epoxidation of allylic alcohols) or β-aminoalcohols (derived from aminoacids) their most usual precursor compounds. We recently described a simple method to prepare both enantiomers of chiral non racemic aziridines based on reactions of N-*p*-tolylsulfinylimines and sulfur ylides[3] (Scheme 1). In this paper, we reported that the stereochemical outcome of the reaction can be inverted by using dimethyloxosulfonium methylide instead of dimethylsulfonium methylide. Moreover, we show for the first time that the best method for removing the sulfinyl group of the N-sulfinylaziridines was by treatment with MeLi at -78°C, which gives not only the corresponding enantiomerically pure aziridine,[4] but also the valuable enantiomerically pure methylsulfoxide.
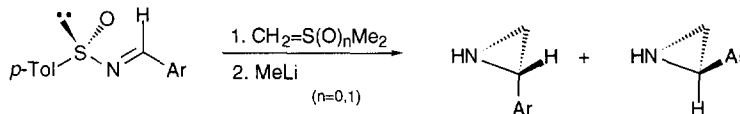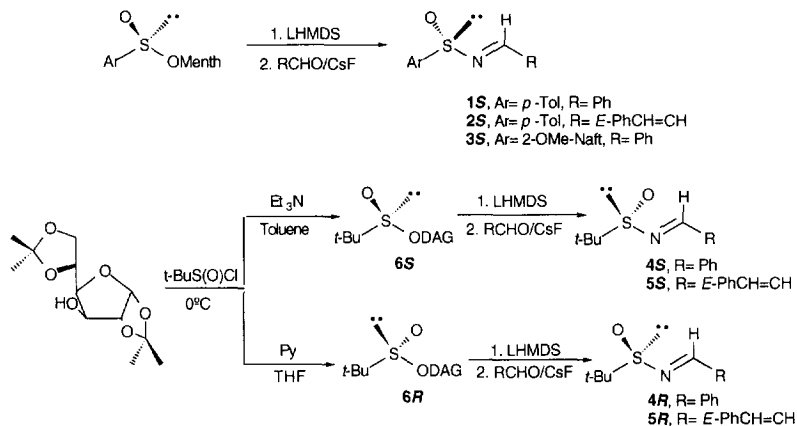


Scheme 1

Nevertheless, the interest of this reaction as a general method to prepare enantiomerically pure aziridines was limited mainly due to its modest diastereoselectivity (de < 50%), which in the case of the N-*p*-tolylsulfinyl-2-phenylaziridine was compensated by the easy separation of both diastereoisomers. Shortly, after this work, a paper appeared by the Davis group on the same reaction.[5] In this paper, where only dimethyloxosulfonium methylide was used as methylene transfer reagent, it was shown that the use of 2-methoxy-1-naphthylsulfinyl group as chiral auxiliary did not improve the diastereoselection of this reaction (de 50%). In the present paper we report our recent studies on the influence of the substituent of the sulfinyl sulfur on the stereochemical results of the aziridination of N-sulfinylimines with either dimethyloxosulfonium methylide or

dimethylsulfonium methylide as methylene transfer reagents. From these studies, we show that the *tert*-butylsulfinyl group is the inducer of chirality of choice for the aziridination reaction. The high stereoselectivity obtained makes this method very attractive for synthetic purposes.

## RESULTS AND DISCUSSION

In order to improve the diastereoselectivity of the aziridination reactions starting from N-sulfinylaldimines a straightforward approach is the change of steric and stereoelectronic nature of the substituent at the sulfinyl sulfur. For this reason, N-sulfinylimines **1-5** with *p*-tolyl, 2-methoxynaphtyl, and a *tert*-butyl group were chosen as representative starting materials. The synthesis of N-sulfinylimines **1-3** was achieved from the appropriated aldehyde and the corresponding arenesulfinate [(1*R*,2*S*,5*R*)-(-)-menthyl (*S*)-*p*-toluenesulfinate or (1*R*,2*S*,5*R*)-(-)-menthyl (*S*)-2-methoxy-1-naphthalenesulfinate[7]] using a known method.[6] For the synthesis of the most interesting N-sulfinylimines **4-5**, having the bulky *tert*-butylsulfinyl group, we applied the recently introduced "*DAG methodology*".[8] Interestingly, starting from a single inducer of chirality (diacetone-*D*-glucose) and following the same synthetic scheme N-sulfinylimines **4S, 5S, 4R** and **5R**, epimers at the sulfinyl sulfur, can be obtained in enantiomerically pure forms by the simple use of triethylamine or pyridine in the first step (Scheme 2).



**1S**, Ar= *p*-Tol, R= Ph
**2S**, Ar= *p*-Tol, R= *E*-PhCH=CH
**3S**, Ar= 2-OMe-Naft, R= Ph

**4S**, R= Ph
**5S**, R= *E*-PhCH=CH

**4R**, R= Ph
**5R**, R= *E*-PhCH=CH

Scheme 2

The synthesis of aziridines **7-11** from N-sulfinylimines **1-5** was done using either dimethylsulphonium methylide (reagent **A**) or dimethyloxosulphonium methylide (reagent **B** or **C**) as methylene transfer reagents, under the best conditions we have previously reported.[3] The results obtained are summarized in Table 1.

Several general remarks can be drawn from this Table. Firstly, it is a general feature for all substrates studied to display an opposite diastereoselection at the newly created C-2 carbon when using reagent **B** instead of **A**. Thus, starting from (*S*$_S$)-N-sulfinylimines, (*S*$_S$,*S*) aziridines are the major isomers with dimethyloxosulfonium methylide (reagent **B**) in toluene, whereas (*S*$_S$,*R*)-aziridines are the major ones with dimethylsulfonium methylide (reagent **A**) in DMSO. Secondly, lower reactivities (longer reaction times) but higher stereoselectivities (higher de) are associated with the use of reagent **B** in toluene. Finally, the high yields of the reactions conducted with the reagent **B** in toluene at room temperature contrast with the rather moderated ones that were obtained in THF as solvent.[5] Moreover, the diastereoselectivity observed in toluene for compound **3S** (66% de and 80% yield, entry 6, Table 1) is also higher to that reported by Davis for a similar substrate in THF (50% de and 51% yield, entry 10 in the table of ref.4) which indicates that toluene is more efficient than THF as solvent for these reactions.

**Table 1**: Reaction of N-sulfinylimines **1-5** with dimethylsulphonium methylide (n=0, reagent **A**) and dimethyloxosulphonium methylide (n=1, reagents **B** and **C**).
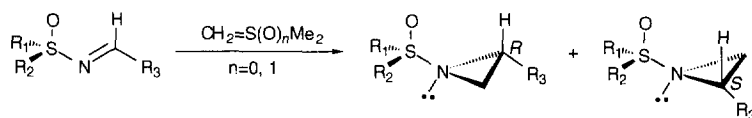


| Entry | $R_1$ | $R_2$ | $R_3$ | Reagent[a] | Time (h) | N-Sulfinyl aziridines | $(2S):(2R)$[b] Ratio[c] | Yield[d] (%) | de (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | p-Tol | .. | Ph | **A** | 2 | **7**[3] | 40:60 | 73 | 20 |
| 2 | p-Tol | .. | Ph | **B** | 48 | **7**[3] | 73:27 | 95 | 46 |
| 3 | p-Tol | .. | (E)PhCH=CH | **A** | 2 | **8** | 42:58 | 82 | 16 |
| 4 | p-Tol | .. | (E)PhCH=CH | **B** | 48 | **8** | 60:40 | 85 | 20 |
| 5 | Naphthyl | .. | Ph | **A** | 48 | **9** | 23:77 | 75 | 54 |
| 6 | Naphthyl | .. | Ph | **B** | 144 | **9** | 83:17 | 80 | 66 |
| 7 | t-Bu | .. | Ph | **A** | 48 | **10** | 15:85 | 70 | 70 |
| 8 | t-Bu | .. | Ph | **B** | 168 | **10** | 95:5 | 85 | 90 |
| 9 | .. | t-Bu | Ph | **B** | 168 | **10** | 5:95 | 85 | 90 |
| 10 | t-Bu | .. | (E)PhCH=CH | **A** | 48 | **11** | 18:82 | 72 | 64 |
| 11 | t-Bu | .. | (E)PhCH=CH | **C** | 72 | **11** | 83:17 | 40 | 66 |

[a]Generated in situ from trimethylsulfonium iodide with NaH in DMSO for **A**, from trimethyloxosulfonium iodide with NaH in toluene for **B** and in THF as solvent with n-BuLi as base for **C**.[9] [b]Configuration at the aziridine carbon. [c]Determined on the crude mixture by ^{1}H NMR. [d]Isolated yields.

With regard to the influence of the substituent at the sulfinyl sulfur on the diastereoselection of the reaction, as it can be seen from Table 1, an increase in the steric hindrance of this substituent is always accompanied with an increase in the diastereoselection. Thus, the stereoselectivity of the reaction was improved when changing the p-tolyl derivative **1S** by the naphthyl derivative **3S** in the reaction with both ylides[10] (compare entries 1 and 2 with 5 and 6 respectively), and this was much more significant in the case of the t-butyl derivatives. Thus, starting from **4S** the de with both ylides **A** and **B** increase up to 70% and 90% respectively (entries 7 and 8). The high de obtained in the reaction of **4S** with the reagent **B**, allowed us to

isolate the enantiomerically pure N-sulfinylaziridine **10(Ss,S)** in 75% yield by a single crystallization (hexane) from the crude mixture, which was not possible in previous cases where a chromatographic separation was always necessary.[3,5,11] As with the *"DAG methodology"* both N-sulfinylimines epimer at the sulfinyl sulfur are accessible, the aziridine **10(Rs,R)**, with the opposite configuration at C-2, was obtained in a similar way (85% yield, 90% de) starting from the N-sulfinylimine **4R** (entry 9, Table 1).

It is worth nothing that α,β-unsaturated sulfinylimines **2** and **5**, with two possible sites of reaction (C=C and C=N) only react by the imine site, even with dimethyloxosulfonium methylide (reagent **B** or **C**), which is reported to react on the C=C bond in the case of α,β-unsaturated carbonyls (yielding cyclopropanes). Moreover, the evolution of these substrates, with R$^2$=($E$)-CH=CH-Ph, shows lower stereoselectivity than the phenylderivatives with both ylides, being this difference higher in the reaction conducted with dimethyloxosulphonium methylide (compare entries 1, 2, 7 and 8 with 3, 4, 10 and 11 respectively).
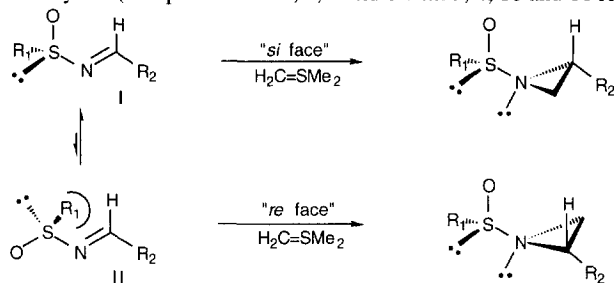


Figure 1

The opposite diastereoselectivity observed when a different methylene transfer reagent is used deserves some comments. In order to rationalize this effect, we assume a similar explanation to that proposed to justify their evolution in reactions with the aldehydic carbonyl group.[12] According to this, the reactions with dimethylsulphonium methylide are processes of kinetic control, whereas those of the dimethyloxosulphonium methylide are subjected to a thermodynamic control.[13] Therefore, the diastereomeric ratio obtained from reagent **A** must be controlled by the relative rates of its attack on the diastereotopic faces of the C=N bond of the N-sulfinylimine, whereas that obtained from reagent **B** must be related to the thermodynamic stability of the diastereomeric addition products. In the first case, the favored attack of the dimethylsulphonium methylide (reagent **A**) on the C=N bond must take place from the less hindered face of the C=N group, which is that supporting the lone electron pair at sulfur in the most populated conformation[14] (Figure 1). The conformational equilibrium around the N-S bond must be shifted towards rotamer **I** (S-O bond in *s-cis* arrangement with respect to N=C) due to steric and electronic grounds. The population of **II** (S-O bond in *s-trans* arrangement) must became lower when the steric size of R$_1$ increases, which agrees with the experimental results (compare entries 1, 5 and 7).[14] In this case, both the low ability of Na$^+$ to be associated and the nature of the solvent (DMSO), able to stabilize cations, suggest a scarce or none role of the association on the stereochemical outcome of the reactions.

In the case of the methyloxosulfonium methylide, the situation is different because the ratio of the diastereomeric N-sulfinylaziridines must be related to the stability of the betainic intermediates. Taking into account the long distance between the two chiral centers, it would be very difficult to justify a significant difference in the stability of both diastereoisomers unless we assume the existence of some factor able to get them become closer. The association of the metal with the sulfinyl oxygen could be this factor.[15] Thus, in Figure 2 are depicted the most stable conformations of diastereomeric betaines, with the three heteroatoms

involved in the association with the Na$^+$. Due to the steric interactions the intermediate **A** -with ($S_S$,$S$) configuration- is more favored than **B** -with ($S_S$,$R$) configuration-, which would explain the predominance of the former in the equilibrium and, therefore, ($S_S$,$S$)-aziridine is the major component of the reaction mixtures.
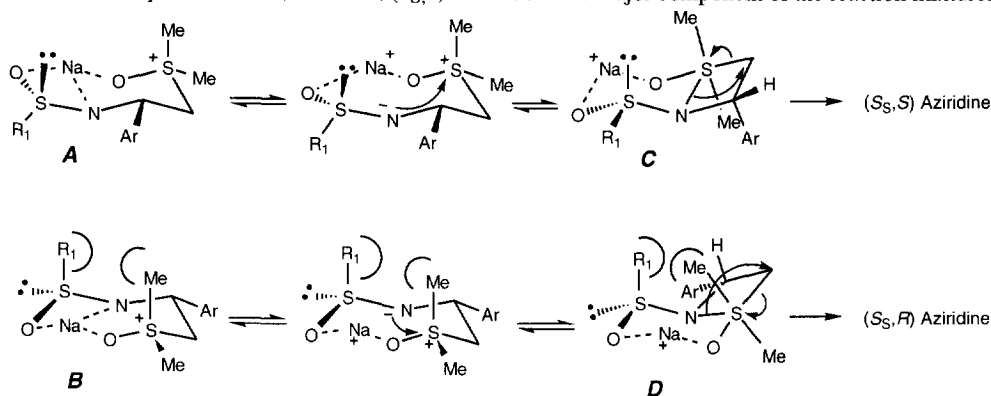


Figure 2

Another alternative explanation would involve the formation of a pentacoordinated 1,2$\lambda^6$-azathietane, similar to the 1,2$\lambda^6$-oxathietanes recently reported by Okazaki et al..[16] The formation of such species could be the result of the evolution indicated in Figure 2. The weakest metal-heteroatom bond (presumably N$^-$...Na$^+$ ) is broken and the nucleophilic nitrogen N$^-$ forms the pentacoordinated species by attack on the oxosulfonium sulfur S$^+$. As we can see, this intermediate displays the oxygen in pseudoequatorial arrangement (instead of the most usual axial position) retaining its association with the metal. As we can see in Figure 2, the intermediate **C** with ($S_S$,$S$ ) configuration, is more stable than the ($S_S$,$R$)-**D**, due to the steric interactions. Whatever the explanation is, the increase of the size of the sulfinyl substituent R$_1$ will determine a greater shifting of the equilibrium towards the most stable species provoking an increasing in the stereoselectivity of the reaction.

## CONCLUSION

In summary, we have evaluated the effect of the increase of the steric hindrance of the substituent at the sulfinyl sulfur in the N-sulfinylimine on the diastereoselectivity of the aziridination reaction. From this study we have shown that the *tert*-butylsulfinyl group is the best chiral auxiliary for the synthesis of enantiomerically pure aziridines. The use of the *"DAG methodology"* allows the synthesis of both epimers of N-sulfinylimines in a short and efficient way. Thus, the diastereoselection of the reaction can be tuned in two ways, the chirality at the sulfinyl sulfur or by the nature of the methylene transfer reagent used, being the former one more efficient. So, both aziridines **10**($S$s,$S$) and **10** ($R$s,$R$) were obtained enantiomerically pure in 75% yield after a single crystalization. These results, associated with our earlier finding that the sulfinyl group can be smoothly removed by the treatment with MeLi, make the method presented here very attractive for synthetic purposes.

## EXPERIMENTAL

Melting points were determined in open capillary tubes on a Gallenkamp apparatus and are not corrected. Routine monitoring of reactions was performed using Merck 60 F254 silica gel, glass supported TLC plates. For flash chromatography, silica gel 60 (230-400 mesh ASTM, E.Merck) was used. Columns were eluted with positive air pressure. Infrared spectra were recorded on a Bomen, Michelson 100, FT IR spectrophotometer. $^1$H NMR spectra were recorded at 200 MHz and $^{13}$C NMR spectra at 50 MHz, on Bruker instruments.

Chemical shifts are reported in ppm , and coupling constants are reported in Hz. High-resolution mass spectra were recorded on a Kratos MS-80-RFA spectrometer. Optical rotations were taken on a Perkin-Elmer 241-MC apparatus. All reactions were run under an atmosphere of dry argon using flame-dried glassware and freshly distilled and dried solvents. The organic extracts were dried over anhydrous sodium sulfate and concentrated in vacuo.

*N-SULFINYLIMINES. GENERAL METHOD:*[5]

To a solution of 3.4 mmol (1.0 equiv) of sulfinate in  dry THF (15 mL) at -78°C, under argon, was added a solution of LHMDS 1.0 M in THF (from 1.5 to 5.0 equiv, depending on the substituent at sulfur in the sulfinate). The mixture was stirred at room temperature (from 3 to 48 hours), until all the starting material was consumed. The reaction was cooled at 0°C and added to a solution of the aldehyde (2.0 to 5.3 equiv) and CsF (0.3 to 2.0 equiv) in THF (10 mL). After stirring at room temperature (from 3 to 48 hours) the reaction mixture was quenched with saturated NH$_4$Cl solution and extracted with ethyl acetate (8x100 mL). The organic layer was washed with brine, dried over Na$_2$SO$_4$,  evaporated under vacuo and purified by silica gel column chromatography (C.C.).

**(+)-(S)-(E)-N-(Benzylidene)-p-toluenesulfinamide, 1(S)**.[5] (C.C.: ethyl acetate:hexane, 1:15); Yield: 90%; m.p. 86-87°; [$\alpha$]$^{20}$D +115 (c. 1.0, CHCl$_3$). Lit.[5] [$\alpha$]$^{20}$D +117 (c. 1.0, CHCl$_3$); $^1$H NMR(CDCl$_3$): δ 8.75 (s, 1H), 7.86 (m, 2H), 7.65 and 7.32 (AA'BB'system, 4H), 7.5 (m, 3H), 2.42 (s,3H ).

**(+)-(S)-(E)-N-(3-E-Phenylpropenylidene)-p-toluenesulfinamide, 2(S)**.[5] (C.C.: ethyl acetate:hexane, 1:10); Yield: 80%; m.p. 110°C; Lit. 112°C; [$\alpha$]$^{20}$D +377 (c. 0.6, CHCl$_3$). Lit.[5] [$\alpha$]$^{20}$D +337 (c. 1.54, CHCl$_3$); $^1$H NMR(CDCl$_3$): δ 8.53 (d, 1H, J=8.9Hz), 7.62-7.25 (m, 9H), 7.26 (d, 1H, J=15.8Hz), 7.05 (dd, 1H, J=15.8, 8.9Hz), 2.39 (s,3H); $^{13}$C NMR(CDCl$_3$): δ 161.4, 146.8, 141.7 134.8, 130.2, 129.8, 128.9, 127.8, 125.4, 124.5, 21.4.

**(+)-(S)-(E)-N-(Benzylidene)-2-methoxy-1-naphthalenesulfinamide, 3(S)**.[5] (C.C.; ethyl acetate:hexane, 1:8); Yield: 75%; m.p. 107-109°C; [$\alpha$]$^{20}$D +107 (c. 1.0, CHCl$_3$); $^1$H NMR(CDCl$_3$): δ 9.07 (s,1H), 8.61 (d, 1H, J=8.5 Hz), 8.02-7.81 (m, 4H), 7.57-7.28 (m, 6H), 4.07 (s, 1H); $^{13}$C NMR(CDCl$_3$): δ 161.7, 157.1, 134.5, 133.9, 132.2, 131.3, 129.3, 129.1, 113.3; IR(CHCl$_3$): υ$_{max}$ 3020, 1610, 1280, 1090 cm$^{-1}$; Anal. Calcd. for C$_{18}$H$_{15}$SO$_2$N : C 69.88%, H 4.89%, N 4.53%, S 10.36%, found: C 69.75%, H 5.12%, N 4.65%, S 10.12%.

**(+)-(S)-(E)-N-(Benzylidene)-tert-butanesulfinamide, 4(S)**. (C.C.: ethyl acetate:hexane, 1:15); Yield 70%; [$\alpha$]$^{20}$D +104 (c. 1.0, CHCl$_3$); $^1$H NMR(CDCl$_3$) : δ 8.59 (s, 1H), 7.87-7.83 (m, 2H), 7.51-7.47 (m, 3H), 1.27 (s, 9H); $^{13}$C NMR(CDCl$_3$) : δ 162.6, 133.9, 132.3, 129.2, 128.8, 57.6, 22.5; IR(CHCl$_3$): υ$_{max}$ : 3030, 2950, 1610, 1580, 1450, 1360, 1160, 1100 cm$^{-1}$.

**(-)-(S)-(E)-N-(Benzylidene)-tert-butanesulfinamide, 4(R)**. Purified  by  silica  gel  column chromatography (ethyl acetate:hexane, 1:15); Yield 50%; [ $\alpha$]$^{20}$D -101 (c. 1.0, CHCl$_3$); Spectral properties identical to 4(S).

**(+)-(S)-(E)-N-(3-E-Phenylpropenylidene)-tert-butanesulfinamide, 5(S)**. (C.C.: ethyl acetate:hexane, 1:9); Yield: 56%; m.p. 48-50°C; [$\alpha$]$^{20}$D +331 (c. 1.4, CHCl$_3$); $^1$H NMR(CDCl$_3$) : δ 8.34 (d, 1H, J=8.7Hz), 7.34-7.51 (m, 5H), 7.21 (d, 1H, J=15.8Hz), 7.05 (dd, 1H, J=15.8, 8.7 Hz), 1.20 (s, 9H); $^{13}$C NMR(CDCl$_3$): δ 163.71, 146.30, 134.92, 130.16, 128.89, 127.83, 127.74, 125.46, 57.49, 22.42; HRMS: Calcd for C$_{13}$H$_{17}$NSO 235.1025, found 235.1222 (5.7 ppm).

*SYNTHESIS OF AZIRIDINES.*

<u>*Method A*</u>*: Aziridination of N-sulfinylimines with dimethylsulfonium methylide in DMSO.* 0.87 mmol (3 equiv) of prewashed NaH was added portionwise to a solution of 0.87 mmol (3 equiv) of trimethylsulfonium iodide in dry DMSO (5 mL). After stirring at room temperature for two hours, 0.29 mmol (1 equiv) of sulfinylimine in DMSO (10 mL), under argon was added and the reaction mixture was stirred at room temperature until all the starting material was consumed, and then poured onto crushed ice and extracted with ether (8x100 mL). The organic layer was washed with brine (100 mL), dried over $Na_2SO_4$ and evaporated under vacuo. The resulting mixture of diastereoisomers was analysed by $^1H$ NMR to determine the ratio on the crude mixture and then separated by silica gel column chromatography.

<u>*Method B*</u>*: Aziridination of N-sulfinylimines with dimethyloxosulfonium methylide in toluene.* 1.43 mmol (3 equiv) of prewashed NaH was added portionwise to a solution of 1.43 mmol (3 equiv) of trimethyloxosulfonium iodide in dry toluene (5 mL). After stirring at room temperature for 2 hours, 0.5 mmol (1 equiv) of N-sulfinylimine in toluene (10 mL), under argon was added. The reaction mixture was stirred at room temperature until all the starting material was consumed, and then poured onto crushed ice and extracted with ethyl acetate (8x100 mL). The organic layer was washed with brine (100 ml), dried over $Na_2SO_4$ and evaporated under vacuo. The resulting mixture of diastereoisomers was analysed by $^1H$ NMR to determine the ratio on the crude mixture and then separated by silica gel column chomatography.

**N-(*p*-Tolylsulfinyl)-2-(2´-phenylvinyl)aziridine, 8(*S*$_S$,*E*,2*S*).** Yellow crystaline solid; m.p. 117.5-118.3ºC; $[\alpha]^{20}_D$ +277 (c. 0.8, CHCl3); $^1H$ NMR(CDCl3): δ 7.62-7.21 (m, 9H), 6.75 (d, 1H, J=15.9Hz), 5.95 (dd, 1H, J=8.0, 15.9Hz), 3.10 (ddd, 1H, J=8.0, 6.9, 4Hz), 2.72 (d, 1H, J=6.9Hz), 2.41 (s, 3H), 1.74 (d, 1H, J=4Hz); $^{13}C$ NMR(CDCl3): δ 141.87, 141.80, 136.11, 133.79, 127.86, 126.18, 129.54, 128.53, 126.25, 124.64, 36.91, 24.63, 21.37.

**N-(*p*-Tolylsulfinyl)-2-(2´-phenylvinyl)aziridine, 8(*S*$_S$,*E*,2*R*).** Yellow crystaline solid; m.p. 61.0-71.6º; $[\alpha]^{20}_D$ -163.7 (0.8, CHCl3); $^1H$ NMR(CDCl3): δ 7.62-7.21 (m, 9H), 6.45 (d, 1H, J=15.9Hz), 3.26 (ddd, 1H, J=8.1, 6.9, 4.14Hz), 2.60 (d, 1H, J=6.9Hz), 2.30(s,3H), 2.22 (d, 1H, J=4.1). $^{13}C$ NMR(CDCl3): δ. 141.85, 141.71, 133.43, 129.48, 128.44, 127.71, 126.14, 125.69, 124.69, 30.70, 21.35.HRMS: Calcd for $C_{17}H_{17}NSO$ 282.97787, found 283.1024.

**N-(2-Methoxy-1-naphthalenesulfinyl)-2-phenylaziridine, 9(*S*$_S$,2*S*).** (Data taken from a mixture of both diastereomers **9(*S*$_S$,2*S*)** and **9(*S*$_S$,2*R*)**). $^1H$-NMR(CDCl3): δ 9.00 (d, 1H, J= 8.6 Hz), 7.95-7.15 (m, 10H), 4.02 (s, 3H), 3.45 (m, 2H), 2.29 (d, 1H, J=3.2 Hz).

**N-(2-Methoxy-1-naphthalenesulfinyl)-2-phenylaziridine, 9(*S*$_S$,2*R*).** (Data taken from a mixture of both diastereomers **9(*S*$_S$,2*S*)** and **9(*S*$_S$,2*R*)**). $^1H$-NMR(CDCl3): δ 9.00 (d, 1H), 7.95-7.15 (m, 10H), 4.32 (dd, 1H, J= 7.0, 4.3 Hz), 3.82 (s, 3H), 2.75 (d, 1H, J=7.0 Hz), 2.35 (d, 1H, J= 4.3 Hz).

**N-(*tert*-Butylsulfinyl)-2-phenylaziridine, 10(*S*$_S$,2*S*).** Solid; m.p. 83-85ºC; $[\alpha]^{20}_D$ +348 (c. 0.8, CHCl3); $^1H$-NMR(CDCl3): δ 7.28-7.24 (m, 5H), 3.12 (dd, 1H, J= 6.4, 4.0 Hz), 2.99 (d, 1H, J= 6.4 Hz), 2.01 (d, 1H, J= 4.0 Hz), 1.30 (s, 9H); $^{13}C$-NMR(CDCl3): δ 137.65, 128.42, 127.68, 126.64, 126.32, 57 38, 34.79, 28.64, 22.77.

**N-(*tert*-Butylsulfinyl)-2-phenylaziridine, 10(*S*$_S$,2*R*).** (Data taken from a mixture of both diastereomers **10(*S*$_S$,2*S*)** and **10(*S*$_S$,2*R*)**). $^1H$ NMR(CDCl3):δ 7.30-7.28(m, 5H), 3.60(dd, 1H, J=4.0, 7.0 Hz), 2.44(d, 1H, J=7.0 Hz), 2.16 (d, 1H, J=4.0 Hz), 1.17 (s, 3H).

**N-(*tert*-Butylsulfinyl)-2-phenylaziridine, 10(*R*$_S$,2*R*).** $[\alpha]^{20}_D$ -320 (0.5, CHCl3); Spectral properties identical to **10(*S*$_S$, 2*S*)**; HRMS: Calcd for $C_{12}H_{17}NSO$ 222.1025, found 223.1031 (0.1 ppm) .

**N-(*tert*-Butylsulfinyl)-2-(2´-phenylvinyl)aziridine, 11(*S*<sub>S</sub>,2*R*).** (Data taken from a mixture of both diastereomers **11(*S*<sub>S</sub>,2*S*)** and **11(*S*<sub>S</sub>,2*R*)**). ^{1}H NMR(CDCl₃): δ 7.20-7.45 (m, 5H), 6.65 (d, 1H, J=15.9Hz), 5.91 (dd, 1H, J=15.9, 8.5Hz), 3.27 (ddd, 1H, J=8.5, 6.7, 3.8Hz), 2.31 (d, 1H, J=6.7Hz), 2.12 (d, 1H, J=3.8Hz), 1.21 (s, 9H).

**N-(*tert*-Butylsulfinyl)-2-(2´-phenylvinyl)aziridine, 11(*S*<sub>S</sub>,2*S*).** (Data taken from a mixture of both diastereomers **11(*S*<sub>S</sub>,2*S*)** and **11(*S*<sub>S</sub>,2*R*)**). ^{1}H NMR(CDCl₃): δ 7.20-7.45 (m, 5H), 6.73 (d, 1H, J=15.9Hz), 5.90 (dd, 1H, J=15.9, 7.48Hz), 2.84 (d, 1H, J=6.7Hz), 2.75 (ddd, 1H, J=7.4, 6.7, 3.8Hz), 1.93 (d, 1H, J=3.8Hz), 1.23 (s, 9H).

## REFERENCES AND NOTES

1. See D. Tanner, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599 and references cited therein.

2. D. Tanner, *Pure and Appl. Chem.* **1993**, *65*, 1319.

3. J.L. García Ruano, I. Fernández, C. Hamdouchi, *Tetrahedron Lett.*, **1995**, *36*, 295.

4. The asignation of the absolute configuration of the major aziridine product made in our previous work (ref. 3) was erroneous. This was due to a typographic error on the sign of the specific rotation, associated to the fact that in the original paper (B.B. Lohray, J.R. Ahuja, *J. Chem. Soc., Chem. Commun.*, **1991**, 97) the configurational assignment of (+)-2-phenylaziridine was erroneous.

5. F.A. Davis, P. Zhou, C-H. Liang, R.E. Reddy, *Tetrahedron:Asymmetry*, **1995**, *6*, 1511.

6. F.A. Davis, R.E. Reddy, J.M. Szewczyk, P.S. Portonovo, *Tetrahedron Lett.*, **1993**, *34*, 6229.

7. S.G. Payne, A.R. Hajipour, K. Prabakaran, *Tetrahedron Lett.*, **1994**, *35*, 645.

8. N. Khiar, I. Fernández, F. Alcudia, *Tetrahedron Lett.*, **1994**, *35*, 5719.

9. In the case of the N-sulfinylimine **5S**, dimethyloxosulfonium methylide was generated in THF with *n*-BuLi as base (reagent **C**). When the reaction was conducted in toluene with NaH as base (reagent **B**) only decomposition products were obtained.

10. In contrast with our findings, Davis reported in ref. 4 that in THF both stereoselectivity and yield decrease when the naphthylsulfinyl group instead of the *p*-tolyl one is used as chiral auxiliary.

11. This is more interesting from a synthetic point of view because the chromatographic purification of the sulfinylaziridines was not possible in all cases. Thus, we could not obtain diastereomerically pure aziridines **9** and **10** by chromatographic methods. As the epimer **10(*S*<sub>S</sub>,*R*)** could not be obtained by crystallization, it was necessary undergo the reaction of **4(*R*)** with benzaldehyde to obtain the N-sulfinylaziridine **10(*R*<sub>S</sub>,*R*)** (precursor of the (*R*)-aziridine) in optical pure form.

12. C.R. Johnson, C.W. Schroeck, J.R. Shanklin, *J. Am. Chem. Soc*, **1973**, *95*, 7424.

13. The higher stability (and therefore lower reactivity) of the Me₂SOCH₂⁻ (reagent **B**) with respect to the Me₂SCH₂⁻ (reagent **A**), together with the steric factors, determine a much easier N-C intramolecular attack (yielding the aziridine) on the sulfonium salt than that on the oxosulfonium salt (in this case, carbon to be attacked is like neopentyl carbon because sulfur is similar to a *t*-butyl group), and a different kind of control is opperative with each methylide.

14. In vinyl sulfoxides, the *s-cis* conformation of the S-O bond has been shown to be more stable than the *s-trans* in thiane S-oxides (see N.L. Allinger, J.A. Hirsch, M.A. Miller, I.J. Tyminski, *J. Am. Chem. Soc.*, **1969**, *91*, 337.). In the case of N-sulfinylimines the antiperiplanar arrangement between the lone electron pair at nitrogen and the sulfinyl oxygen must be favored because it exhibits the lowest electronic repulsion. The conformation displaying the R₁ group in *s-trans* arrangement with respect to the N=C bond could also be considered (specially if size of R₁ is large) but the attack of the reagent **A** on the less hindered face would yield the same diastereoisomer that **I**.

15. Despite the low ability of the Na⁺ to become coordinated, the low polarity of the solvent used (toluene) would allow its association.

16. F. Ohno, T. Kawashima and R. Okazaki, *J. Am. Chem. Soc.*, **1996**, *118*, 697. In this paper it is suggested that this kind of pentacoordinated species could be involved as intermediates in the reactions of dimethylsulphonium methylide with carbonyl compounds.