Ring opening reactions of 2-trialkylsilylaziridines

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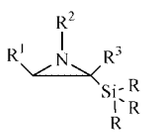
2-Trialkylsilylaziridines do not readily undergo nucleophilic ring opening without electrophilic assistance. In the presence of strong acids protonation at the nitrogen is followed by nucleophilic attack α to the silicon. With non-nucleophilic counterions, the protonated aziridine can be obtained. *N*-Alkylation gives the aziridinium salt, which also undergoes α-cleavage. However, the presence of a 3-phenyl substituent gives a stable aziridinium salt that undergoes nucleophilic attack β to the silicon. Reaction of 2-trialkylsilylaziridines with trialkylsilyl halides usually leads to α-cleavage, however, desilylation to give the enamine is also observed. Fluorodesilylation of the 2-trialkylsilylaziridine is not straightforward and only occurred readily when a 2-ethoxycarbonyl group was present. Fluorodesilylation followed by attack on a carbonyl was only observed when very dry samples of fluoride ions were employed.

Introduction

2-Trialkylsilylepoxides undergo regiospecific and stereospecific transformations to give vinyl halides,[1] enol ethers[2] and carbonyl compounds[3] and are thus important synthetic intermediates. Although the ring opening reactions of 2-trialkylsilylepoxides have been studied extensively, little is known of the selectivity of ring opening of 2-trialkylsilylaziridines. We have recently published the synthesis of 2-trialkylsilylaziridines, **1**, with a range of substituents, including hydrogen, on the ring



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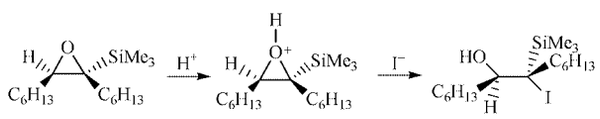
nitrogen and carbons.[4] In this paper we report our studies on the synthetic versatility of silylaziridines and in particular their ring opening reactions with electrophilic and nucleophilic reagents.

Nozaki, Hudrlik, Whitham and their co-workers[5–9] have shown that nucleophilic attack on 2-trialkylsilylepoxides generally occurs at the carbon α to the silicon accompanied by α-opening of the ring. The expected S_N1 like β-opening involving stabilisation of the β-carbocation by the silicon is not observed since the geometry of the ring prevents overlap of the C–Si bond with the developing empty p orbital. However, other substituents in the ring may overwhelm the influence of the silicon leading to other ring opened products. For example, a 2-trialkylsilylepoxide with one phenyl group in the 3 position still undergoes nucleophilic attack α to the silicon, however, the presence of two phenyl groups at the 3 position leads to formation of a carbocation α to the phenyl groups and β to the silicon.[10] Similarly, with conformationally rigid 2-trialkylsilylepoxides, the bias towards *trans* diaxial ring opening results in hydride attack leading to cleavage of either C–O bond.[11] This high regioselectivity of nucleophilic attack of 2-trialkylsilylepoxides α to the silicon is maintained even when the oxygen is protonated, as shown in Scheme 1, circumstances where S_N1 ring opening may be thought to be predominant.

Simple aziridines undergo ring opening only if the nitrogen is protonated or alkylated. Substitution on the ring carbons leads to a more "S_N1-susceptible" carbon atom (the more substituted site) and a more "S_N2-susceptible" carbon atom (the least



Scheme 1

hindered site).[12] In such cases the regiochemistry depends upon the reaction conditions and the nature of the nucleophile. The ring opening of aziridines is enhanced if there is an electron withdrawing group on the nitrogen. In such cases quaternisation of the nitrogen is not necessary, however, the regiochemistry of ring opening still depends upon the substituents on the ring carbons, the conditions and the nucleophile.[13] Ring opening reactions of aziridines have been recently reviewed by Tanner.[14]

These observations suggest that the presence of a 2-trialkylsilyl substituent in an aziridine should favour attack α to the silicon if the reaction proceeds *via* an S_N2 type route. However, attack β to the silicon will be favoured if an S_N1 route with a late transition state is favoured, such that stabilisation involving the C–Si bond can be achieved.

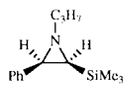
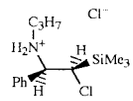
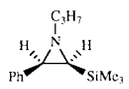
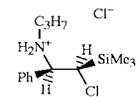
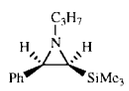
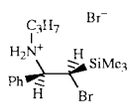
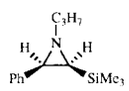
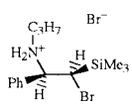
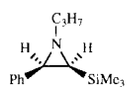
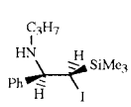
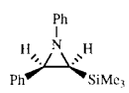
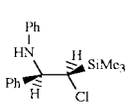
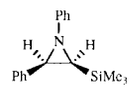
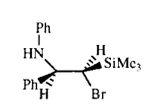
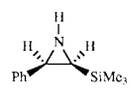
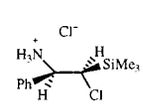
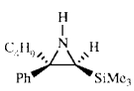
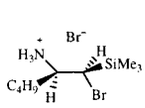
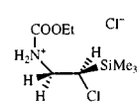
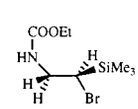
Results and discussion

Ring opening with nucleophilic reagents

Trialkylsilylepoxides do not undergo ring opening by direct nucleophilic attack with ease. In many cases such reactions only proceed with electrophilic assistance. For example, *cis*-1-trimethylsilyloct-1-ene oxide undergoes ring opening α to the silicon with pyrrolidine or morpholine in the presence of alumina.[15] However, trialkylsilylepoxides can be transformed into the corresponding β-hydroxytrialkylsilanes using organometallic reagents, such as organocuprates.[16] We found that trialkylsilylaziridines demonstrated a similar resistance to ring opening. *N*-Alkyl- and *N*-phenyl-2-trimethylsilylaziridines, with and without substituents in the 3 position did not react with lithium aluminium hydride, sodium methoxide, lithium di-*n*-butylcuprate (in the presence and absence of BF_3) or pyrrolidine in the presence of alumina.

The presence of an ethoxycarbonyl group in the 2 position of aziridines has been used by Baldwin and co-workers to activate them towards ring opening with organometallic[17] and Wittig[18] reagents. Unfortunately, we found that 2-ethoxycarbonyl-1-phenyl-2-trimethylsilylaziridine did not undergo ring opening

Table 1 Addition of hydrogen halides to a range of 2-trimethylsilylaziridines

Reactant	Hydrogen halide	Product	Method	Yield
	HCl		A	46%
	HCl		B	76%
	HBr		A	83%
	HBr		B	72%
	HI		A	[a]
	HCl		B	60%
	HBr		B	76%
 3	HCl		B	96%
 4	HBr		B	65%
 5	HCl		A	55%
	HBr		B	52%

[a] Crude yield 74%, decomposed on purification.

with methylmagnesium iodide, lithium di-*n*-butylcuprate, aniline, benzylamine or diethyl malonate anion. Any reaction observed was usually the result of attack of the nucleophile at the carbonyl group.

Aziridines can be activated to nucleophilic ring opening by placing an electron withdrawing group on the nitrogen. For example, *N*-ethoxycarbonylaziridines undergo facile ring opening with aniline.[13] Again, 1-ethoxycarbonyl-2-trimethylsilylaziridine failed to undergo ring opening with the range of nucleophiles previously mentioned. When reaction was observed it usually involved loss of the ethoxycarbonyl group. The inability of 2-trimethylsilylaziridines to undergo ring opening reactions under conditions where non-silyl substituted aziridines have been shown to react suggest the silicon is in some way preventing attack at the aziridine ring. Attack at the 2 position, may be hindered by the bulky silicon atom, however, this does not prevent attack at the 3 position. The failure to observe such attack may be due to an electronic effect of the silicon, which destabilises the transition state of S_N2 substitution in the β position.

Ring opening reactions with hydrogen halides

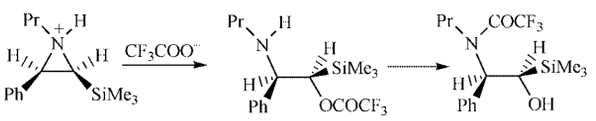
Whilst trialkylsilylaziridines are difficult to ring open by purely nucleophilic means, prior protonation leads to facile ring opening. Addition of hydrogen halides to 2-trialkylsilylaziridines generally leads regiospecifically to the corresponding β-haloamine, as shown in Table 1. The same product was obtained irrespective of whether a solution of the hydrogen halide in water (Method A) was used or the pure hydrogen halide in carbon tetrachloride (Method B). Presumably protonation of the nitrogen is followed by attack of the nucleophile α to the silicon. Depending upon the acid, the conditions and the nature of the group attached to the nitrogen either the free amine or

the ammonium salt could be obtained. Treatment of the β-haloamine with base gave back the aziridine with retention of configuration, confirming that the reaction is stereoselective.

Reaction of *trans*-1,3-diphenyl-2-trimethylsilylaziridine with any hydrogen halide led to a polymeric product, even at −78 °C. This is probably the result of nucleophilic attack of the product amine on the protonated aziridine. Addition of hydrogen chloride and hydrogen bromide to 2-ethoxycarbonyl-1-phenyl-2-trimethylsilylaziridine by either method gave only aniline hydrochloride formed by cleavage of both C–N bonds.

Ring opening reactions with other acids

Reaction of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine with trifluoroacetic acid gave the corresponding protonated aziridinium salt. This could be achieved in a range of solvents at room temperature without further nucleophilic attack of the trifluoroacetate ion. Treatment of the product with base gave back the free aziridine. However, if the aziridinium salt was refluxed in methanol or hexane, nucleophilic attack of the anion α to the silicon was observed. This was followed by acyl exchange leading to the isolated product **7**, as shown in Scheme 2.



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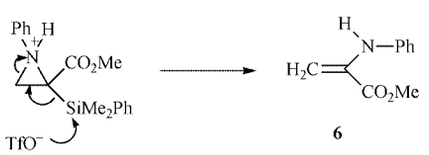
Scheme 2

When 1-ethoxycarbonyl-2-trimethylsilylaziridine and 2-ethoxycarbonyl-1-phenyl-2-trimethylsilylaziridine were treated with trifluoroacetic acid, the protonated aziridine was not observed, only the product of α-ring opening. In these cases acyl exchange did not occur. Under identical conditions, *cis*- or *trans*-1,3-diphenyl-2-trimethylsilylaziridine gave only a polymeric product.

A similar picture emerged with trifluoromethanesulfonic acid. *cis*-3-Phenyl-1-propyl-2-trimethylsilylaziridine gave a protonated aziridinium salt, whereas, 1-ethoxycarbonyl-2-trimethylsilylaziridine gave the product of α addition. Reaction of 2-methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine with trifluoromethanesulfonic acid gave the enamine **6**, arising from attack of the nucleophile at the silicon atom, as shown in Scheme 3.



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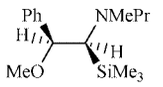
Scheme 3

The reaction of aziridines with acid to give stable aziridinium salts can be used to resolve chiral aziridines. Protonation of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine using the homochiral acid (*S*)-(+)-1,1′-binaphthyl-2,2′-diylhydrogen phosphate gave a white solid that could be fractionally recrystallised to give samples of the two diastereoisomeric salts. Reaction with triethylamine gave the free aziridines as a pair of optical isomers. The optical rotation was found to be ±92°.

Ring opening reactions with methylating agents

Methylation of 2-trialkylsilylaziridines using methyl iodide was unsuccessful, however, the alkyl aziridinium salt of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine could be prepared in moderate yield using methyl trifluoromethanesulfonate. Methylation is much slower than protonation and thus is more susceptible to side reactions such as ring opening or desilylation. 1-Ethoxycarbonyl-2-trimethylsilylaziridine gave the product of α ring opening with methyl trifluoromethanesulfonate, whereas methylation of *cis*-1,3-diphenyl-2-trimethylsilylaziridine led to desilylation.

The *cis*-1-methyl-3-phenyl-1-propyl-2-trimethylsilylaziridinium triflate was relatively stable, enabling us to examine its ring opening reactions. Boiling the aziridinium salt in methanol led to the β ring opened product of solvolysis, **8**. Treatment



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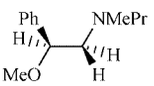

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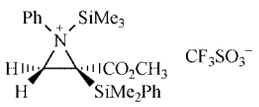

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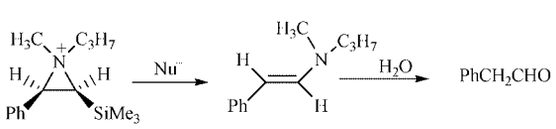
with sodium methoxide in methanol led to the corresponding desilylated product, **9**.

Compound **8** arises from an S_N1 like process involving an intermediate/activated complex with substantial carbocation character adjacent to the phenyl group and β to the silicon. Such behaviour has been reported by Leonard for the solvolysis of unsymmetrically carbon-substituted aziridinium ions.[19] They found that treatment with methoxide ion led to the products expected for an S_N2 type pathway. However, we found that reaction of the 2-trimethylsilylaziridinium salt with methoxide ion led to desilylation. This could occur before or after ring opening, however, we would favour initial desilylation since no silylated ring opened products were observed in the reaction mixture during the reaction. We found no evidence of an S_N2 type reaction, only an S_N1 type ring opening of the desilylated aziridine which leads to the expected product under the direction of the phenyl group.

The solvolysis of aziridinium salts is the only example of nucleophilic attack β to the silicon atom that we have observed with 2-trialkylsilylaziridines. We have been unable to find any examples in the literature of a mechanistic difference between *N*-methylated aziridinium salts and *N*-protonated aziridinium salts. Indeed, we have found examples of protonated and methylated 2,2-dialkylaziridines exhibiting attack at either centre, depending upon the conditions.[20] The delicate balance between stabilisation of the incipient carbocation and attack at the α carbon is illustrated by the reaction of 1-ethoxycarbonyl-2-trimethylsilylaziridine with methyl trifluoromethylsulfonate, which only gave the products of α addition. In this case, despite potential β stabilisation by the silicon, the formation of a primary carbocation, leads to a preference for S_N2 substitution. The reaction of *cis*-1-methyl-3-phenyl-1-propyl-2-trimethylsilylaziridinium triflate with other nucleophiles such as methylmagnesium bromide, halides and cyanide led to a complex mixture of desilylated products. However, phenylacetaldehyde could be detected in up to 34% yield. This is presumably formed by desilylation to give the enamine followed by hydrolysis, as shown in Scheme 4.

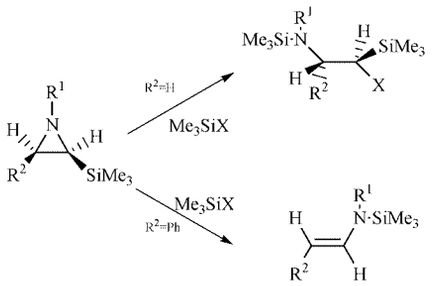


Scheme 4

Ring opening reactions with trialkylsilylhalides

The reaction of 1-ethoxycarbonyl-2-trimethylsilylaziridine and 1-phenyl-2-trimethylsilylaziridine with trialkylsilyl bromide,

chloride and iodide gave the corresponding β-haloamines. This was achieved using either stoichiometric or catalytic quantities of the reagent. Presumably *N*-silylation to give the salt is followed by attack of the iodide at the carbon α to the silicon. However, *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine and *cis* and *trans*-1,3-diphenyl-2-trimethylsilylaziridine reacted with trialkylsilylhalides to give a *trans*-*N*-silylenamine, as shown in Scheme 5.



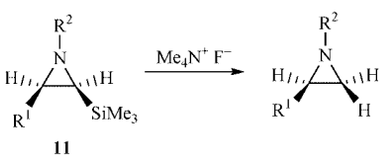
Scheme 5

This difference in behaviour highlights again the directing effect of the phenyl group in these systems. The aromatic group stabilises the development of an adjacent positive charge, which in turn, favours desilylation. No reaction was observed with other trimethylsilyl halides, azides or cyanides.

The reaction of trimethylsilyltrifluoromethanesulfonate with 2-ethoxycarbonyl-1-phenyl-2-trimethylsilylaziridine did not lead to ring opening but gave the silylated aziridinium salt **10**.

Fluorodesilylation reactions of 2-trialkylsilylaziridines

trans-1,3-Diphenyl-2-trimethylsilylaziridine reacts with fluoride ion to give the desilylated product rather than a ring opened product, as shown in Scheme 6. Such behaviour is well



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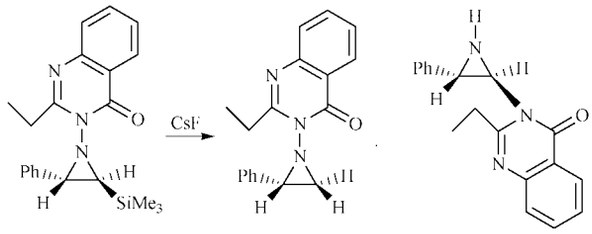
Scheme 6

documented for the corresponding 2-trialkylsilylepoxides.[21] However, we found that fluorodesilylation of other 2-trialkylsilylaziridines was not an easy reaction to perform and this was the only simple aziridine, **11**, (R^1 = H or Ph, R^2 = Ph, Pr or CO_2Et) to undergo such a reaction. Alkali metal fluorides and tetrabutylammonium fluoride were employed under a range of conditions, including rigorous drying,[22–25] however no reaction was observed.

Desilylation of 2-ethoxycarbonyl-1-phenyl-2-trimethylsilylaziridine potentially leads to a stabilised anion and thus might be expected to occur more readily than with simple aziridines. In fact fluorodesilylation of 2-ethoxycarbonyl-1-phenyl-2-trimethylsilylaziridine took place easily and rigorous drying was not necessary. Replacement of the trialkylsilyl group with a dialkylphenylsilyl group has been shown to promote desilylation.[26] We thus prepared 2-ethoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine. This underwent fluorodesilylation even more readily than the trimethylsilyl analogue.

Atkinson has desilylated the 2-trimethylsilylaziridine **12** using caesium fluoride.[27] Under his conditions two products were obtained, as shown in Scheme 7, the simple desilylation product, **13**, and a rearranged compound, **14**, formed *via* the intermediate azirine. This was confirmed by repeating the reaction in the presence of benzaldehyde, which traps the intermediate aziridinyl carbanion. We found that formation of such carbanions from the simple aziridines, (**11**, R^1 = H or Ph,

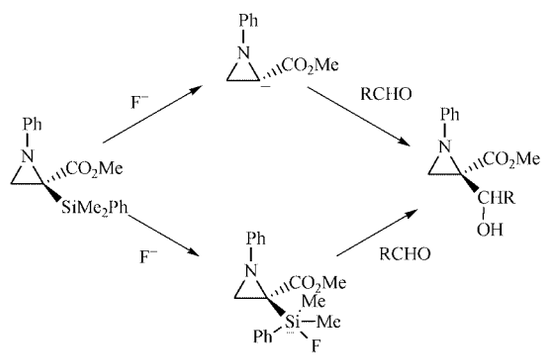


12 **13** **14**

Scheme 7

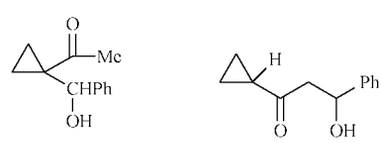
R^2 = Ph, Pr or CO_2Et) with subsequent trapping by a carbonyl compound proved impossible, as was observed for the replacement with a hydrogen. Whilst fluorodesilylation of 2-ethoxycarbonyl-1-phenyl-2-dimethylphenylsilylaziridine followed by protonation was quite simple, subsequent trapping with a carbonyl compound was not straightforward. This was because of preferential protonation by water that was present in the fluoride source. However, when very dry sources of tetrabutylammonium fluoride[23–25] were employed, reaction with hexanal or benzaldehyde could be observed. The product was a mixture of the free alcohol and the corresponding silyl ether. In both cases a 1 : 1 mixture of diastereoisomers was obtained. Reaction was not observed with ketones, including cyclohexanone, which led to aldol products. Presumably in such cases nucleophilic attack at the carbonyl is hindered such that the aziridinyl anion or fluoride ion preferentially acts as a base. Similarly, no addition was observed with the hindered aldehyde 2,2-dimethylethanal or ethanal and propanal which underwent trimerization.

Two mechanisms can be proposed for the desilylation and concomitant reaction with the aldehyde or proton, as shown in Scheme 8. Firstly fluoride ion could attack the silicon to form



Scheme 8

trialkylsilyl fluoride and a free aziridinyl carbanion. This then attacks the carbonyl compound. Alternatively, fluoride ion could attack the silicon to generate a pentacoordinate silicon, which subsequently attacks the carbonyl compound. Similar free carbanion[28] and pentacoordinate[29] mechanisms have been proposed for fluorodesilylation of allyltrialkylsilanes. A nucleophilic pentacoordinate silicon species has also been suggested for group transfer polymerisation.[30] Paquette *et al.* have shown that fluorodesilylation of 1-trimethylsilylcyclopropane methyl ketone in the presence of benzaldehyde leads to a mixture of **15** and **16**. This suggests the formation of the free carbanion which undergoes equilibration.[31]



15 **16**

We found that both 2-ethoxycarbonyl-1-phenyl-2-dimethylphenylsilylaziridine and 2-ethoxycarbonyl-1-phenyl-2-trimethylsilylaziridine underwent desilylation in the presence of a proton donor, although the latter reaction occurred more slowly. However whilst 2-ethoxycarbonyl-1-phenyl-2-dimethylphenylsilylaziridine underwent desilylation with attack on a carbonyl compound, no such reaction was observed with 2-ethoxycarbonyl-1-phenyl-2-trimethylsilylaziridine. If reaction occurred *via* a free carbanion, the same intermediate aziridinyl anion would be formed in each case so the absence of reaction with the carbonyl is hard to explain. This suggests reaction occurs *via* a pentacoordinate species.

Experimental

Melting points were determined on a Buchi 510 melting point apparatus and are uncorrected. Infrared spectra were obtained as Nujol mulls or thin films using sodium chloride plates or as KBr discs on a Pye Unicam SP1050 or a Nicolet 205 FT-IR spectrometer. NMR spectra were recorded as solutions in deuterochloroform with tetramethylsilane as internal standard on a JEOL FX 90Q or a JEOL EX 400 NMR spectrometer (J values are given in Hz). Mass spectra were obtained using a Cresta MS 30 instrument or a VG20-250 quadrupole instrument.

Ring opening with hydrogen halides

1-Chloro-2-phenyl-2-propylamino-1-trimethylsilylethane hydrochloride. Method A; the reaction was carried out using aqueous hydrogen chloride (36% w/v) (0.60 ml, 5.66 mmol) and *cis*-3-pheny1-1-propyl-2-trimethylsilylaziridine (0.44 g, 1.89 mmol) in dichloromethane (10 ml). The reaction mixture afforded 1-chloro-2-phenyl-2-propylamino-1-trimethylsilylethane hydrochloride on filtration and washing with hexane (0.23 g, 45.7%), mp 196–198 °C; ν_{max} (Nujol)/cm^{-1} 2540–2270, 1590, 1250, 850, 740 and 700; δ_H (400 MHz, $CDCl_3$, Me_4Si) −0.26 (9H, s, $SiMe_3$), 0.79 (3H, t, CH_3/Pr), 1.82 (2H, m, CH_2CH_3/Pr), 2.60 (12H, m, CH_2N/Pr), 4.27 (2H, d, J 4.7, ring H's) and 7.26–7.68 (7H, m, Ph, NH_2^+ exchangeable with D_2O); δ_C (100 MHz, $CDCl_3$, Me_4Si) −3.20 ($SiMe_3$), 11.20 (CH_3/Pr), 18.84 ($CH_2CH_2CH_3$), 46.99 (N–CH_2), 50.50 (CCl), 66.87 (Ph–CN), 128.97 (C-2 & C-6/Ph), 129.54 (C-4/Ph), 129.83 (C-3 & C-5/Ph) and 130.58 (C-1/Ph); m/z (EI) 254 (M − HCl − CH_3, 0.27%), 211 (M − NHC_3H_7 − HCl, 0.28), 190 ($C_{11}H_{16}$NSi, 2.46), 160 ($C_{11}H_{14}N$, 2.36), 148 (PhCHNHPr, 100), 73 ($SiMe_3$, 21), 36 (HCl, 13) and 28 (Si, 22) (Found: C, 54.0; H, 9.3; N, 4.6. $C_{14}H_{25}Cl_2NSi$ requires C, 54.2; H, 9.4; N, 4.5%).

1-Chloro-2-phenyl-2-propylamino-1-trimethylsilylethane hydrochloride. Method B; the reaction was carried out using excess gaseous hydrogen chloride and *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (0.30 g, 1.29 mmol) in carbon tetrachloride (5 ml). On filtration and washing with hexane, the reaction mixture gave white l-chloro-2-phenyl-2-propylamino-1-trimethylsilylethane hydrochloride (0.3 g, 76%). The product was confirmed by comparison of spectra with those of an authentic sample.

1-Bromo-2-phenyl-2-propylamino-1-trimethylsilylethane hydrobromide. Method A; the reaction was carried out using an aqueous solution of hydrogen bromide (46% w/v) (1.3 ml, 7.46 mmol), *cis*-3-phenyl-1-propy1-2-trimethylsilylaziridine (0.58 g, 2.49 mmol) in dichloromethane (10 ml). The reaction afforded white l-bromo-2-phenyl-2-propylamino-1-trimethylsilylethane hydrobromide on filtration and thorough washing with hexane (0.65 g, 83%), mp 198–200 °C; ν_{max} (Nujol)/cm^{-1} 2520–2270, 1580, 1220, 1100, 850, 765 and 700; δ_H (400 MHz, $CDCl_3$, Me_4Si) −0.20 (9H, s, $SiMe_3$), 0.75 (3H, t, CH_3/Pr), 1.70 (2H, sextet, CH_2CH$_3$/Pr), 2.65 (2H, m, CH_2N/Pr), 4.30 (2H, s, ring opened H's) and 7.20–7.74 (7H, m, Ph, NH_2^+, exchangeable with D_2O); δ_C (100 MHz, $CDCl_3$, Me_4Si) −2.47 ($SiMe_3$), 11.03 (CH_3/Pr), 18.79 (CH_2CH_3Pr), 42.62 (CBr), 47.16 (NCH_2), 67.04 (PhCN), 129.48 (C-2 & C-6/Ph), 129.83 (C-4/Ph), 130.69 (C-3 & C-5/Ph) and 131.73 (C-1/Ph); m/z (EI) 298 (M − CH_3 − HBr, 0.41%), 255 (M − NHC_3H_7 − HBr, 0.46), 190 ($C_{11}H_{16}$NSi, 14.6), 160 ($C_{11}H_{14}N$, 13.6), 148 (PhCHNHPr, 100), 80 (HBr, 25) and 73 ($SiMe_3$, 74) (Found: C, 42.5; H, 7.3; N, 3.6. $C_{14}H_{25}Br_2NSi$ requires C, 42.2; H, 7.3; N, 3.5%).

1-Bromo-2-phenyl-2-propylamino-1-trimethylsilylethane hydrobromide. Method B; gaseous hydrogen bromide was sparged very slowly through a solution of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (0.30 g, 1.29 mmol) in carbon tetrachloride (5 ml). The reaction was monitored by ^{1}H NMR analysis. After sparging for 5 min, the reaction mixture afforded 1-bromo-2-phenyl-2-propylamino-1-trimethylsilylethane hydrobromide (0.4 g, 72%) on filtration and washing with hexane. The product was confirmed by comparison of its spectra with those of an authentic sample.

1-Iodo-2-phenyl-2-propylamino-1-trimethylsilylethane. An aqueous solution of hydrogen iodide (57% w/v) (2.2 ml, 9.59 mmol) was added dropwise to *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (0.75 g, 3.20 mmol) in a 25 ml, 3-necked flask. The solution was stirred at room temperature ($3\frac{1}{2}$ h). Dichloromethane (10 ml) was added and the solution was washed with a saturated solution of sodium hydrogen carbonate. The organic layer was extracted with dichloromethane and again washed with sodium hydrogen carbonate solution. A brown viscous semi-solid was obtained after drying over anhydrous magnesium sulfate and removal of the solvent. Attempts to purify the product, 1-iodo-2-phenyl-2-propylamino-1-trimethylsilylethane, using a silica column failed due to its decomposition; ν_{max}(neat)/cm^{-1} 3390, 1625, 1510–1400, 1340, 1270, 1200–1050, 1075, 1030, 900–850, 770, 760 and 710–670; δ_H (400 MHz, $CDCl_3$, Me_4Si) −0.12 (9H, s, $SiMe_3$), 0.90 (3H, t, CH_3/Pr), 1.95 (2H, sextet, CH_2CH$_3$/Pr), 2.80 (2H, m, CH_2N), 4.39 (1H, d, J_{AB} 12.0, CH), 4.75 (1H, d, J_{AB} 12.0, CH) and 7.43–8.00 (6H, m, Ph & 1H from NH exchangeable with D_2O); δ_C (100 MHz, $CDCl_3$, Me_4Si) −1.09 ($SiMe_3$), 11.03 (CH_3/Pr), 19.30 ($NCH_2CH_2CH_3$), 23.32 (*C*I), 47.97 (N*C*H$_2$), 68.13 (Ph–CN), 129.54 (C-2 & C-3/Ph), 130.06 (C-4/Ph), 130.98 (C-3 & C-5/Ph) and 131.38 (C-1/Ph).

2-Anilino-1-chloro-2-phenyl-1-trimethylsilylethane. The reaction was carried out using gaseous hydrogen chloride and *cis*-l,3-diphenyl-2-trimethylsilylaziridine (0.25 g, 0.93 mmol) in carbon tetrachloride (5 ml). After 3 min, the reaction mixture gave solid white 2-anilino-l-chloro-2-phenyl-l-trimethylsilylethane hydrochloride on filtration and washing with hexane (0.l5 g, 38%), mp 179–181 °C; ν_{max} (Nujol)/cm^{-1} 2750–2400, 1610–1590, 1500, 1250, 860, 830, 800 and 700; δ_H (400 MHz, $CDCl_3$, Me_4Si) −0.20 (9H, s, $SiMe_3$), 4.50 (2H, s, ring-opened H's) and 7.00–7.60 (12H, m, Ph–NH_2, exchangeable with D_2O); δ_C (100 MHz, $CDCl_3$, Me_4Si) −2.99 ($SiMe_3$), 49.40 (C–$SiMe_3$), 73.65 (CPh), 124.95 (C-2 & C-6/Ph), 128.39 (C-2 & C-6/NPh), 128.91 (C-4/Ph), 129.54 (C-4/NPh), 130.00 (C-3 & C-5/Ph), 131.09 (C-3 & C-5/NPh), 131.67 (C-1/Ph) and 133.97 (C-1/NPh); m/z (EI) 303 ($C_{17}H_{23}Cl_2NSi$, 4.2%), 267 ($C_{17}H_{21}NSi$, 1.2), 194 ($C_{17}H_{21}NSi$–$SiMe_3$ or $C_{14}H_{12}N$, 5.2), 182 (PhCH=NHPh, 100), 77 (Ph, 9.8) and 73 ($SiMe_3$, 20.9) (Found: C, 67.0; H, 7.5; N, 4.5. $C_{17}H_{23}Cl_2NSi$ requires C, 67.0; H, 7.6; N, 4.6%).

The supernatant was concentrated to dryness to give solid light-brown 2-anilino-1-chloro-2-phenyl-1-trimethylsilylethane on washing with hexane (0.12 g, 60%), mp 75–76 °C; ν_{max} (Nujol)/cm^{-1} 3420, 3100–3020, 2960–2840, 1600, 1510, 1450, 1430, 1320, 1250, 920–700 and 800–700; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.04 (9H, s, $SiMe_3$), 3.60 (1H, d, J 3.9, ring-opened H's), 4.70 (1H, d, J 3.9, ring opened H's) and 6.40–7.30 (11H, m,

$PhNH_2^+$, exchangeable with D_2O); δ_C (100 MHz, $CDCl_3$, Me_4Si) −2.64 ($SiMe_3$), 57.19 (C–$SiMe_3$), 58.83 (CPh), 113.63 (C-2 & C-6/Ph), 117.94 (C-2 & C-6/NPh), 126.96 (C-4/Ph), 127.48 (C-4/ NPh), 128.40 (C-3 & C-5/Ph), 129.20 (C-3 & C-5/ NPh) and 140.98 (C-1/Ph) (Found: C, 67.1; H, 7.3; N, 4.6. $C_{17}H_{22}ClNSi$ requires C, 67.2; H, 7.3; N, 4.6%).

2-Anilino-1-bromo-2-phenyl-1-trimethylsilylethane. The reaction was carried out using gaseous hydrogen bromide and *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (0.20 g, 0.75 mmol) in carbon tetrachloride (5 ml). After 8 min, the pale yellow solution was concentrated to dryness and washed with hexane to afford a cream-coloured solid, 2-anilino-l-bromo-2-phenyl-1-trimethylsilylethane (0.20 g, 76%), mp 101–102 °C; ν_{max} (Nujol)/cm^{-1} 3400, 1600, 1580, 1250 and 915-680; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.20 (9H, s, $SiMe_3$) 3.70 (1H, d, *J* 3.0, ring-opened H's), 4.70 (1H, d, *J* 3.0, ring-opened H's) and 6.50–7.30 (11H, m, Ph–NH); δ_C (100 MHz, $CDCl_3$, Me_4Si) −2.07 ($SiMe_3$), 52.27 (*C*$SiMe_3$), 58.36 (C-Ph), 113.80 (C-2 & C-6/Ph), 118.11 (C-2 & C-6/NPh), 126.85 (C-4/Ph), 127.43 (C-4/NPh), 128.39 (C-3 & C-5/Ph), 129.25 (C-3 & C-5/NPh), 141.26 (C-1/Ph) and 145.45 (C-1/NPh); *m/z* (EI) 347 ($C_{17}H_{22}BrNSi$, 3.8%), 267 (M − HBr or $C_{17}H_{21}NSi$, 2.2), 194 ($C_{17}H_{21}NSi$ − $SiMe_3$ or $C_{14}H_{21}N$, 6.7), 182 (PhCH=NHPh, 100), 77 (Ph, 8.6) and 73 ($SiMe_3$, 22.3) (Found: C, 58.5; H, 6.3; N, 4.0. $C_{17}H_{22}BrNSi$ requires C, 58.6; H, 6.4; N, 4.0%).

2-Amino-1-chloro-2-phenyl-1-trimethylsilylethane hydrochloride. *cis*-3-Phenyl-2-trimethylsilylaziridine (0.1 g, 0.524 mmol) was placed in a 5 ml NMR tube with 1 ml $CDCl_3$ and hydrogen chloride was passed through the solution. After 1 second of purging, the NMR spectrum of the reaction mixture indicated the presence of an aziridinium salt and also that of a ring opened product. After several seconds of purging with the gas, the product consisted entirely of the ring opened derivative. The solvent was evaporated and the remaining off-white solid was recrystallized from 50 : 50, ether–chloroform to give white crystals of 2-amino-1-chloro-2-phenyl-1-trimethylsilylethane hydrochloride (0.133 g, 0.504 mmol, 96.2%). The solid decomposed without melting on heating; δ_H (400 MHz, $CDCl_3$, Me_4Si) −0.18 (9H, s, $SiMe_3$), 3.85 (1H, d, *J* 10.5, C*H*Si), 4.28 (1H, d, *J* 10.5, C*H*Ph), 6.33 (3H, s, NH_3, exchangeable with H_2O) and 7.25–7.40 (5H, m, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) −3.0 ($SiMe_3$), 51.2 (*C*$SiMe_3$), 61.0 (*C*Ph), 128.8, 129.4, 130.0 and 133.9 (Ph).

2-Amino-1-bromo-1-trimethylsilylhexane hydrobromide. The reaction was carried out as before, using 0.2 g of *trans*-3-butyl-2-trimethylsilylaziridine and gaseous hydrogen bromide. The proton NMR spectrum of the product obtained from the reaction is consistent with 2-amino-1-bromo-1-trimethylsilylhexane hydrobromide. An attempt to purify this product further resulted in decomposition; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.24 (9H, s, $SiMe_3$), 1.62–1.95 (9H, m, $CH_3CH_2CH_2CH_2$), 4.00 (1H, d, *J* 2.0, C*H*Br), 4.36 (1H, dt, *J* 2.0 and 6, C*H*N) and 7.92 (3H, s, NH_3).

Ethyl *N*-(2-chloro-2-trimethylsilylethyl)carbamate hydrochloride. 1-Ethoxycarbonyl-2-trimethylsilylaziridine (0.3 g, 1.60 mmol) was placed in a 5 mm NMR tube with 1 ml of deuterochloroform and the tube cooled in an ice bath. Hydrogen chloride was passed through the solution until all of the aziridine had been consumed, the reaction being followed by proton NMR spectroscopy. On evaporation of the solvent, a brown oil was obtained which was purified by column chromatography on silica using 3 : 10 ether–hexane as the eluent. A colourless oil was obtained which was insoluble in hexane. This yielded, after several recrystallization steps, pure, well defined crystals of the ring opened product, ethyl *N*-(2-chloro-2-trimethylsilylethyl)carbamate hydrochloride (0.23 g, 0.885 mmol, 55%); δ_H (100 MHz, $CDCl_3$, Me_4Si) −0.008 (9H, s, $SiMe_3$), 1.08 (3H, CH_3), 3.10–3.96 (3H, m, CH_2CH) and 5.02 (2H, br s, NH_2); δ_C (400 MHz, $CDCl_3$, Me_4Si) −3.5 ($SiMe_3$), 14.6 (CH_3), 44.3 (CSi), 51.4 (CN), 60.9 (CH_2O) and 156.4 (C=O) (Found: C, 36.8; H, 6.9; N, 5.3. $C_8H_{19}NO_2SiCl_2$ requires C, 36.9; H, 7.3; N 5.4%).

Ethyl *N*-(2-bromo-2-trimethylsilylethyl)carbamate. This reaction was carried out using the same procedure as for the ring opening reaction of 1-ethoxycarbonyl-2-trimethylsilylaziridine with hydrogen chloride to give the ring opened carbamate product in 52% yield; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.11 (9H, s, $SiMe_3$), 1.21 (3H, t, CH_3), 3.24–3.80 (3H, m, CH_2CHSi), 4.09 (2H, q, CH_2O) and 7.12 (1H, br s, NH); δ_C (400 MHz, $CDCl_3$, Me_4Si) −3.2 ($SiMe_3$), 14.4 (CH_3), 43.7 (CSi), 44.0 (CH_2N), 60.8 (CH_2O) and 156.2 (C=O) (Found: C, 35.9; H, 6.8; N, 5.2. $C_8H_{18}NO_2SiBr$ requires C, 35.8; H, 6.8; N, 5.2%).

Reaction of 2-ethoxycarbonyl-1-phenyl-2-triethylsilylaziridine with hydrogen chloride and hydrogen bromide. 2-Ethoxycarbonyl-1-phenyl-2-triethylsilylaziridine (0.1 g, 0.00343 mmol) was dissolved in 1 ml dry ether and hydrogen chloride or hydrogen bromide was passed through the solution for a few seconds. The mixture was evaporated leaving a brown oil. This was purified by column chromatography using 10 : 1 pentane–ether as the eluent. The only product which could be recovered was a white solid which could be identified as aniline hydrochloride by NMR spectroscopy.

Ring opening reactions with other acids

***cis*-3-Phenyl-1-propyl-2-trimethylsilylaziridinium trifluoroacetate.** A solution of trifluoroacetic acid (0.25 g, 2.10 mmol) in diethyl ether (2 ml) was cooled in an ice–methanol bath at −11 °C. A pre-cooled solution of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (0.50 g, 2.10 mmol) in diethyl ether (5 ml) was added dropwise to the trifluoroacetic acid solution. The mixture was stirred under nitrogen at −11 °C ($\frac{1}{2}$ h). The reaction mixture was allowed to warm up to room temperature and stirred for another $\frac{1}{2}$ h at this temperature. The reaction mixture was concentrated to dryness to give *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridinium trifluoroacetate as a yellow oil (98% based on ^1H NMR); ν_{max}(neat)/cm^{-1} 3300–2800, 1700, 1210–1130, 850, 730 and 700; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.21 (9H, s, $SiMe_3$), 1.22 (3H, t, CH_3/Pr), 2.13 (2H, m, CH_2CH_3/Pr), 2.52 (1H, d, *J* 9.5, ring H), 3.49 (2H, m, CH_2N), 4.48 (1H, d, *J* 9.5, ring H), 7.65 (5H, m, Ph) and 8.40 (1H, broad singlet, NH exchangeable with D_2O); δ_C (100 MHz, $CDCl_3$, Me_4Si) −3.62 ($SiMe_3$), 9.71 (CH_3/Pr), 20.16 (CH_2CH_3/Pr), 43.74 (*C*H$SiMe_3$), 50.71 (CHPh), 58.65 (CH_2N), 126.15, 127.91, 128.91 and 129.48 (C's/Ph), 157.87, 159.65, 161.43 and 163.20 (CF_3COO) (Found: C, 55.1; H, 6.8; N, 3.8. $C_{16}H_{24}F_3NO_2Si$ requires C, 55.3; H, 7.0; N, 4.0%).

The reaction was carried out using deuterated chloroform, dimethoxyethane, methanol and hexane–diethyl ether (11 : 1). All systems gave *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridinium trifluoroacetate.

2-(*N*-Propyltrifluoroacetamido)-2-phenyl-1-trimethylsilylethanol. A solution of trifluoroacetic acid (0.25 g, 2.10 mmol) in diethyl ether (2 ml) was added to a solution of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (0.25 g, 2.10 mmol) in diethyl ether (5 ml). The reaction mixture was heated under reflux at 60 °C (1 h) and was concentrated to dryness to yield white 2-(*N*-propyltrifluoroacetamido)-2-phenyl-1-trimethylsilylethanol (13.5%), mp 115–116 °C; ν_{max} (Nujol)/cm^{-1} 3150, 1675, 1640, 1140, 850, 765 and 720; δ_H (400 MHz, $CDCl_3$, Me_4Si) −0.27 (9H, s, $SiMe_3$), 0.84 (3H, t, CH_3/Pr), 1.70 (2H, m, CH_2CH_3/Pr), 2.50 (2H, m, CH_2N), 3.84 (1H, d, *J* 12.0, ring opened H's), 4.20 (1H, d, *J* 12.0, ring opened H's) and 7.47 (6H, broad

singlet, Ph & OH, exchangeable with D_2O); δ_C (100 MHz, $CDCl_3$, Me_4Si) −3.79 ($SiMe_3$), 10.86 (CH_3/Pr), 19.24 (CH_2-CH_3/Pr), 46.82 (C-Ph), 66.12 (NCH_2), 67.33 (CF_3), 128.85 (C-2 & C-6/Ph), 129.60 (C-4/Ph), 130.17 (C-3 & C-5/Ph), 131.95 (C-1/Ph) and 161.00 (C=O); δ_F (400 MHz, $CDCl_3$) −76.39 (s); *m*/*z* (EI) 177 (PhCH–$CHSiMe_3$, 12%), 148 (PhCHNHPr, 100), 77 (Ph), 73 ($SiMe_3$, 40), 28 (Si, 47) (Found: C, 55.1; H, 7.4; N, 4.2. $C_{16}H_{24}F_3NO_2Si$ requires C, 55.3; H, 7.0; N, 4.0%).

Ethyl *N*-(2-trifluoroacetyl-2-trimethylsilylethyl)carbamate. The reaction was carried out using 1-ethoxycarbonyl-2-trimethylsilylaziridine (0.1 g, 0.535 mmol) and trifluoroacetic acid (0.6 g, 0.04 ml, 0.535 mmol) leading quantitatively (by NMR spectroscopy) to the ring opened product, ethyl *N*-(2-trifluoroacetyl-2-trimethylsilyl)carbamate; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.07 (9H, s, Me_3Si), 1.23 (2H, t, CH_3), 3.41 (1H, d, *J* 8.30, NCH_aH_b), 3.49 (1H, d, *J* 4.88, NCH_aH_b), 4.06 (2H, t, CH_2CH_3), 4.99 (1H, dd, *J* 8.30 and 4.88, C*H*$SiMe_3$) and 5.90 (1H, br s, NH); δ_C (100 MHz, $CDCl_3$, Me_4Si) −4.2 (Me_3Si), 14.2 (CH_3), 41.7 (NCH_2), 61.1 (CH_2CH_3), 74.2 (CSi) 119.4 (q, CF_3) and 156.8 (C=O); *m*/*z* (EI) 301 (M^+, 0.2%) 229 (2.9%)/230/231 (9:2:1, $M^+ - SiMe_3$ or CO_2Et), 188 ($M^+ - O_2CCF_3$, 1.9%), 116 (44.9%)/117/118 (9:2:1), 101 (83.2%)/102/103 (77:11:7), 73 ($SiMe_3$ or CO_2Et, 86.8%), 69 (55.6%)/70/71 (88:6:5, CF_3), 59 (38.6) and 29 (Et, 100.0%).

Methyl 2-anilino-1-trifluoroacetyl-1-triethylsilylpropanoate. The reaction was carried out using 2-methoxycarbonyl-l-phenyl-2-triethylsilylaziridine (0.11 g, 0.378 mmol) and trifluoroacetic acid (0.043 g, 0.378 mmol). The major product from this reaction was the ring opened species, methyl 2-anilino-1-trifluoroacetyl-1-triethylsilylpropanoate which began to decompose within a few hours; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.56–0.62 (6H, m) and 0.9–1.0 (9H, m), ($SiEt_3$), 2.49 (1H, s, NCH_aH_b), 2.84 (1H, s, NCH_aH_b), 3.45 (3H, s, CH_3) and 6.85–7.29 (5H, m, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) 3.2 (3 × $SiCH_2$-CH_3), 7.9 (3 × $SiCH_2CH_3$), 35.9 (NCH_2), 52.7 (CH_3), 73.4 (*C*$OCOCF_3$), 120.9, 123.6, 128.7 and 148.1 (Ph) and 171.2 (C=O).

***cis*-3-Phenyl-1-propyl-2-trimethylsilylaziridinium trifluoromethanesulfonate.** Trifluoromethanesulfonic acid (0.13 g, 0.86 mmol) was syringed dropwise into a solution of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (0.20 g, 0.86 mmol) in methanol (1 ml). A yellow solution was obtained after heating under reflux at 65 °C (2 h). The product was confirmed by comparison of its spectra with those of an authentic sample.

Ethyl *N*-(2-trifluoromethanesulfonyl-2-trimethylsilylethyl)-carbamate. The reaction was carried out using 1-ethoxycarbonyl-2-trimethylsilylaziridine (0.1 g, 0.535 mmol) and trifluoromethanesulfonic acid (0.047 ml, 0.535 mmol). NMR spectroscopy indicated immediate and quantitative conversion to ethyl *N*-(2-trifluoromethanesulfonyl-2-trimethylsilylethyl)-carbamate; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.12 (9H, s, Me_3Si), 1.39 (3H, t, CH_3), 3.78 (1H, dd, *J* 19.76 and 12.21, NH_aH_b), 4.16 (1H, dd, *J* 19.67 and 10.74, NH_aH_b), 4.57 (2H, q, CH_2CH_3), 5.01 (1H, dd, *J* 12.21 and 10.74, C*H*Si) and 9.96 (1H, s, NH); δ_C (100 MHz, $CDCl_3$, Me_4Si) −5.2 (Me_3Si), 13.7 (CH_3), 45.2 (NCH_2), 72.9 (CH_2CH_3), 81.9 (CSi), 119.6 (q, CF_3) and 165.7 (C=O).

Methyl 2-anilinopropenoate. 2-Methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine, (0.05 g, 0.161 mmol) was dissolved under nitrogen in 0.5 ml of deuterochloroform, in a 5 mm NMR tube, and cooled in an ice–methanol bath. Trifluoromethanesulfonic acid (0.0241 g, 0.161 mmol) was syringed slowly into the tube. The reaction was followed by NMR spectroscopy and complete conversion to methyl 2-anilinopropenoate was observed after 2 hours. The product was confirmed by comparison of its spectra with those of an authentic sample.

***cis*-3-Phenyl-1-propyl-2-trimethylsilylaziridinium (*S*)-(+)-1,1′-binaphthyl-2,2′-diyl phosphate.** A solution of *cis*-3-pheny1-1-propyl-2-trimethylsilylaziridine (0.20 g, 0.86 mmol) in methanol (0.5 ml) was added to a suspension of (*S*)-(+)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate ((+)-BNPA) (0.30 g, 0.86 mmol) in methanol (2 ml) under nitrogen. The pale reaction mixture was allowed to stir at room temperature (2 h). The solution was concentrated to dryness to give a white crystalline solid (0.40 g, 44%). Fractional crystallisation from absolute ethanol afforded enantiomeric *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridiniun (*S*)-(+)-1,1′-binaphthyl-2,2′-diyl phosphate; δ_H (400 MHz, $CDCl_3$, Me_4Si) −0.30 (9H, s, $SiMe_3$), 0.60 (3H, t, CH_3/Pr), 1.20–1.90 (3H, m (including one d at 1.70, *J* 9.0), CH_2/Pr and ring opened H's), 2.50–2.90 (2H, m, CH_2N), 3.80 (1H, d, *J* 9.0, ring opened H's), 7.00–8.00 (18H, m, Ph (5H), BNPA (12H) and N^+H (1H)); δ_C (100 MHz, $CDCl_3$, Me_4Si) −2.41 ($SiMe_3$), 10.63 (CH_3/Pr), 20.34 (CH_2CH_3/Pr), 40.90 (N–CH_2), 49.00 (*C*$SiMe_3$), 59.34 (CPh), 121.96, 124.54, 125.87, 127.01, 127.24, 128.39, 129.94, 130.98, 132.53, 149.19 and 149.53 (C's/aromatic rings).

(+)-*cis*-3-Phenyl-1-propyl-2-trimethylsilylaziridine. A solution of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridiniun (*S*)-(+)-1,1′-binaphthyl-2,2′-diyl phosphate (0.10 g, 0.17 mmol) in dichloromethane (3 ml) was shaken with triethylamine (3 ml). The mixture was left to stand ($\frac{1}{4}$ h). On addition of hexane (5 ml), the reaction mixture afforded a white precipitate, which was removed by filtration. The filtrate was concentrated to dryness to give (+)-*cis*-1-propyl-2-trimethylsilyl-3-phenylaziridine (0.038 g, 0.16 mmol). The product was confirmed by comparison of its spectra with those of an authentic sample.

The angular rotation at 19 °C and path length, 1 dm, (sodium D line as reference) for a solution of 0.76 g of (+)-*cis*-1-propyl-2-trimethylsilyl-3-phenylaziridine in 100 ml ethanol was measured as $[a]_{589}^{19} = +92.5°$.

***cis*-1-Methyl-3-phenyl-1-propyl-2-trimethylsilylaziridinium trifluoromethanesulfonate.** Methyl trifluoromethanesulfonate (0.46 g, 2.80 mmol) was syringed dropwise into a solution of *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (0.65 g, 2.80 mmol) in carbon tetrachloride (1.5 ml) at room temperature under nitrogen. The solution was vigorously stirred and a white precipitate was formed instantaneously. The slurry was allowed to stand (16 h) and the white solid was filtered off and washed with cold carbon tetrachloride and hexane successively. This gave *cis*-1-methyl-3-phenyl-1-propyl-2-trimethylsilylaziridinium trifluoromethanesulfonate (0.70 g, 58%), mp 122–124 °C; ν_{max} (Nujol)/cm^{-1} 1280, 1160, 1040, 850, 750 and 700; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.30 (9H, s, $SiMe_3$), 1.00 (3H, t, CH_3/Pr), 1.90 (2H, sextet, CH_2CH_3/Pr), 2.27 (3H, s, $CH_3/CF_3OSO_2CH_3$), 3.10 (1H, d, *J* 10.5, ring H), 3.50 (2H, m, CH_2N), 4.70 (1H, d, *J* 10.5, ring H) and 7.43 (5H, m, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) −0.75 ($SiMe_3$), 10.17 (CH_3/Pr), 19.01 (CH_2CH_3/Pr), 40.44 (NCH_3), 49.01 ($CHSiMe_3$), 58.65 (CH–Ph), 67.67 (NCH_2), 100.24, 114.49, 128.68 and 142.92 ($CF_3SO_3^-$), 127.24 (C-2 & C-6/Ph), 129.31 (C-4/Ph), 129.71 (C-3 & C-5/Ph) and 130.58 (C-1/Ph); *m*/*z* (EI) 175 ($M - SiMe_3 - CF_3OSO_2$, 53%), 146 ($M - SiMe_3 - CF_3OSO_2 - C_2H_5$, 68), 91 ($PhCH_2$, 24), 77 (Ph, 100) and 73 ($SiMe_3$, 59) (Found: C, 47.9; H, 6.6; N, 3.5; $C_{16}H_{26}F_3NO_3SSi$ requires C, 48.3; H, 6.6; N, 3.5%).

The specific conductance of a solution of the product (0.0387 g) in ethanol (10 ml) was measured using a stainless steel cell and gave a *k* value of $3.96 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 298.4 K.

Ethyl *N*-(2-triflato-2-trimethylsilylethyl)-*N*-methylcarbamate. This was prepared using 1-ethoxycarbonyl-2-trimethylsilyl-

aziridine (0.13 g, 0.695 mmol) and methyl trifluoromethanesulfonic acid (0.115 g, 0.079 ml, 0.695 mmol). The ring opened product was formed in almost quantitative yield by NMR spectroscopy; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.42 (9H, s, Me_3Si), 1.49 (3H, t, CH_3), 2.90 (3H, s, NMe), 3.37 (1H, d, *J* 10.2, NCH_aCH_b), 3.39 (1H, d, *J* 7.1, NCH_aH_b), 4.31 (2H, q, CH_2CH_3), 4.91 (2H, dd, *J* 7.1 and 10.2, C*H*Si). The geminal coupling constant is observed to be zero; δ_C (100 MHz, $CDCl_3$, Me_4Si) −5.1 (Me_3Si), 13.7 (CH_3), 31.2 (MeN), 50.8 (NCH_2), 72.7 (CH_2CH_3), 79.6 (CSi), 120 (q, CF_3), 162.9 (C=O).

2-Methoxy-*N*-methyl-2-phenyl-*N*-propyl-2-trimethylsilylethylamine. A solution of *cis*-1-propyl-2-trimethylsilyl-3-phenyl-*N*-methylaziridinium trifluoromethanesulfonate (0.59 g, 1.49 mmol) in methanol (5 ml) was heated under reflux at 65 °C, using a condenser fitted with a calcium chloride tube. After $4\frac{1}{2}$ h, water (10 ml) was added to the cooled mixture and extracted with diethyl ether (3 × 10 ml). The ethereal solution was dried over anhydrous magnesium sulfate. The filtered solution was concentrated to dryness to afford a pale yellow liquid, 2-methoxy-*N*-methyl-2-phenyl-*N*-propyl-2-trimethylsilylethylamine (0.21 g, 51%); one spot obtained by TLC using hexane as eluent; ν_{max} (neat)/cm^{-1} 3100–2800, 1490, 1450, 1250, 1085, 950, 835 and 760–700; δ_H (400 MHz, $CDCl_3$, Me_4Si) −0.19 (9H, s, $SiMe_3$), 0.85 (3H, t, CH_3/Pr), 1.17–1.87 (2H, m, CH_2CH_3/Pr), 2.47–2.87 (3H, s, N–CH_3), (2H, m + obscured d, NCH_2 and $CHSiMe_3$), 3.07 (3H, s, OCH_3), 3.39 (1H, d, *J* 10.0, CH(OMe)) and 7.30 (5H, s, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) −0.63 ($SiMe_3$), 11.50 (CH_3/Pr), 21.37 (CH_2CH_3/Pr), 40.50 (N–CH_3), 55.44 (OCH_3), 66.61 (NCH_2), 62.85 (CN($SiMe_3$)), 84.10 (CPh), 126.32 (C-2 & C-6/Ph), 127.76 (C-4/Ph), 128.28 (C-3 & C-5/Ph) and 139.77 (C-1/Ph); *m*/*z* (EI) 247 (M − CH_3OH, 4.0%), 206 (N − $SiMe_3$, 6.7), 158 (C_3H_7 − $N^+(CH_3)$=$CHSiMe_3$, 100), 130 ($CH_3N^+(CH_3)$=$CHSiMe_3$, 16.0), 77 (Ph, 1.0), 73 ($SiMe_3$, 4.0) and 28 (Si, 2.0) (Found: C, 68.8; H, 10.3; N, 4.4. $C_{16}H_{29}ONSi$ requires C, 68.8; H, 10.5; N, 5.0%).

2-Methoxy-*N*-methyl-2-phenyl-*N*-propylethylamine. A solution of sodium methoxide (0.07 g, 1.28 mmol) in methanol (0.5 ml) was added dropwise to a solution of *cis*-1-propyl-2-trimethylsilyl-3-phenyl-*N*-methylaziridinium trifluoromethanesulfonate (0.51 g, 1.28 mmol) in methanol (5 ml). The reaction mixture was heated under reflux at 65 °C ($1\frac{1}{4}$ h) using a condenser fitted with a calcium chloride tube. The yellow reaction mixture was washed with distilled water (10 ml) and extracted with diethyl ether (3 × 10 ml). The organic extracts were again washed with distilled water (2 × 30 ml) and dried over anhydrous magnesium sulfate. The filtered solution was concentrated to dryness to afford a yellow liquid containing unreacted aziridinium salt. The residual aziridinium salt was precipitated using hexane, was filtered off and washed with hexane (0.02 g). The filtrate and washings were concentrated to dryness to afford a yellow liquid, 2-methoxy-*N*-methyl-2-phenyl-*N*-propylethylamine (0.14 g, 53%); ν_{max} (neat)/cm^{-1} 3100–3025, 2960–2900, 2870–2800, 1490–1450, 1105, 755 and 700; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.90 (3H, t, CH_3/Pr), 1.20–1.80 (2H, m, CH_2CH_3/Pr), 2.30–2.90 (4H, m, ring-opened CH_2 and CH_2N/Pr), 3.1 (3H, s, N–CH_3), 3.20 (3H, s, OCH_3), 4.20–4.40 (1H, dd, OCH) and 7.30 (5H, s, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) 11.84 (CH_3/Pr), 20.10 (CH_2CH_3/Pr), 43.08 (N–CH_3), 56.76 (OCH_3), 60.26 (N–CH_2/Pr), 64.57 (–C(OMe)–CH_2N–), 82.15 (CH(OMe)), 126.73 (C-2 & C-6/Ph), 127.65 (C-4/Ph), 128.39 (C-3 & C-5/Ph) and 141.09 (C-1/Ph); *m*/*z* (EI) 176 (M − OCH_3, 1.4%), 175 (M − CH_3OH, 2.7), 162 (M − OCH_3 − C_2H_4, 6.2), 146 (M − CH_3OH, 4.4), 121 (PhCHOCH_3, 3.5), 105 (PhCHOH, 5.1), 104 (PhCH=CH_3, 5.3), 91 (PhCH_2, 11), 86 ($CH_2N(CH_3)$Pr, 85.3), 77 (Ph, 9.9), 73 (CH_3OCH_2–CH=N, 3.7), 44 (C_3H_8 or CH_3N=$^+CH_3$, 40.2) and 43 (C_3H_7, 5.0) (Found: C, 75.2; H, 10.5; N 6.7. $C_{13}H_{21}ON$ requires C, 75.3; H, 10.2; N, 6.8%).

Ethyl *N*-(2-bromo-2-trimethylsilylethyl)-*N*-trimethylsilylcarbamate. 1-Ethoxycarbonyl-2-trimethylsilylaziridine (0.1 g, 0.535 mmol) was placed in a 5 mm NMR tube with dry deuterochloroform, under nitrogen and the tube was cooled in an ice bath. Trimethylsilyl bromide (0.082 g, 0.0707 ml, 0.535 mmol) was syringed slowly into the sealed tube. An attempt to purify the product resulted in decomposition, however, NMR spectra indicated that almost complete conversion to the ring opened product, ethyl *N*-(2-bromo-2-trimethylsilylethyl)-*N*-trimethylsilylcarbamate had been achieved. The product was confirmed by comparison of its spectra with those of an authentic sample.

Ethyl *N*-(2-iodo-2-trimethylsilylethyl)-*N*-trimethysilylcarbamate. This reaction was carried out as before using l-ethoxycarbonyl-2-trimethylsilylaziridine (0.1 g, 0.535 mmol) and trimethylsilyl iodide (0.107 g, 0.0761 ml, 0.535 mmol). Again, almost complete conversion to the ring opened product, ethyl *N*-(2-iodo-2-trimethylsilylethyl)-*N*-trimethylsilylcarbamate was achieved, but this could not be purified further; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.26 (9H, s, Me_3SiC), 0.41 (9H s, Me_3SiN), 1.36 (3H, t, CH_3), 3.05–3.40 (2H, m, CH_2N) and 4.02 (2H, q, CH_2O); δ_C (100 MHz, $CDCl_3$, Me_4Si) −2.3 (Me_3SiC), 0.7 (Me_3SiN), 14.2 (CH_3CH_2), 21.8 (CI), 47.4 (NCH_2), 60.7 (OCH_2) and 157.2 (C=O).

Ethyl *N*-(2-chloro-2-trimethylsilylethyl)carbamate hydrochloride. This reaction was carried out as before using 1-ethoxycarbonyl-2-trimethylsilylaziridine (0.1 g, 0.535 mmol) and trimethylsilyl chloride (0.058 g, 0.068 ml, 0.535 mmol). However, the reaction was much slower. Treatment of 1-ethoxycarbonyl-2-trimethylsilylaziridine with trimethylsilyl chloride for several months eventually led to the formation of the hydrogen chloride ring opened product as determined by comparison of the NMR spectra with those of an authentic sample.

***trans*-(*N*-Trimethylsilyl-*N*-propylamino)phenylstyrene.** A solution of *cis*-1-propyl-2-trimethylsilyl-3-phenylaziridine (0.10 g, 0.43 mmol) in deuterated chloroform (3 ml) was syringed in a 5 mm NMR tube under nitrogen. A solution of trimethylsilyl iodide (0.08 g, 0.43 mmol) in deuterated chloroform (0.2 ml) was added dropwise to the solution of aziridine under nitrogen. The NMR tube was shaken thoroughly and left to stand at room temperature to give a yellowish-brown solution of *trans*-(*N*-trimethylsilyl-*N*-propylamino)phenylstyrene (95% as determined by ^{1}H NMR); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.23 (9H, s, $SiMe_3$), 0.70 (3H, t, CH_3/Pr), 1.60 (2H, sextet, CH_2CH_3/Pr), 3.10 (2H, t, CH_2N), 5.30 (1H, d, *J* 14.0, ring opened H's), 6.90 (1H, d, *J* 14.0, ring opened H's) and 7.15 (5H, s, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) 5.50 (N–$SiMe_3$), 11.66 (CH_3/Pr), 21.14 (CH_2/Pr), 46.76 (CH_2–N), 99.67 (=CHPh), 123.22 (C-4/Ph), 123.45 (C-2 & C-6/Ph), 128.34 (C-3 & C-5/Ph), 135.57 ($CHNSiMe_3$) and 139.88 (C-1/Ph).

Attempted purification by column chromatography and distillation on a bigger scale using a Kugelrohr apparatus only gave products of decomposition.

The reaction was also carried out using *cis*-1-propyl-2-trimethylsilyl-3-phenylaziridine (0.10 g, 0.43 mmol) and catalytic quantities of trimethylsilyl iodide (0.02 g, 0.06 mmol). The reaction mixture was analysed by ^{1}H NMR spectroscopy at regular intervals (every $\frac{1}{4}$ h). After 1 h, the reaction mixture afforded *trans*-(*N*-trimethylsilyl-*N*-propylamino)-1-phenylstyrene (96% as determined by ^{1}H NMR). The product was confirmed by comparison of spectra with those of an authentic sample.

***trans*-(*N*-Trimethylsilyl-*N*-phenylamino)phenylstyrene.** The reaction was carried out using *cis*-1,3-diphenyl-2-trimethylsilylaziridine (0.12 g, 0.44 mmol) and trimethylsilyl iodide (0.09 g, 0.44 mmol). The reaction mixture was analysed by ^{1}H NMR spectroscopy at $\frac{1}{4}$ h intervals. After $1\frac{1}{2}$ h, the reaction mixture afforded a yellowish-brown solution containing *trans*-(*N*-

trimethylsilyl-*N*-phenylamino)phenylstyrene (75% as determined by ^{1}H NMR); δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.20 (9H, s, $SiMe_3$), 5.10 (1H, d, *J* 14.0) and 6.50–8.00 (1H, d, *J* 14.0 and, 10H, m, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) 5.51 ($NSiMe_3$), 113.34 (=CHPh), 126.38, 127.34, 128.34, 128.85, 129.03 and 129.25 (Ph C's), 130.12 (=CHN), 142.81 and 145.86 (C-1/Ph's). Attempted purification by chromatography using a silica column and distillation on a bigger scale using a Kugelrohr apparatus only gave products of decomposition.

The reaction was also carried out using *trans*-1,3-diphenyl-2-trimethylsilylaziridine (0.09 g, 0.33 mmol) and trimethylsilyl iodide (0.07 g, 0.33 mmol). After 3 min, the reaction mixture afforded a yellowish-brown solution containing *trans*-(*N*-trimethylsilyl-*N*-phenylamino)phenylstyrene (98% as determined by ^{1}H NMR). The product was characterised by comparison of spectra with those of an authentic sample.

2-Methoxycarbonyl-2-dimethylphenylsilyl-1-phenyl-1-trimethylsilylaziridinium trifluoromethanesulfonate. This reaction was carried out using 0.05 g (0.161 mmol) 2-methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine and 0.036 g (0.031 ml, 0.161 mmol) trimethylsilyltrifluoromethanesulfonic acid. Complete conversion to 2-methoxycarbonyl-2-dimethylphenylsilyl-1-phenyl-1-trimethylsilylaziridinium trifluoromethanesulfonate was observed. The product could not be isolated owing to decomposition on exposure to air; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.12 and 0.44 (6H, 2 × s, Me_2Si), 0.52 (9H, s, Me_3SiN), 2.53 (1H, s, NCH_aH_b), 2.94 (1H, s, NCH_aH_b), 3.51 (3H, t, CH_3) and 6.84–7.59 (10H, m, NPh and SiPh); δ_C (100 MHz, $CDCl_3$, Me_4Si) −3.6 and −3.4 (Me_2Si), 0.9 (Me_3SiN), 36.5 (CH_2), 39.8 (CSi), 50.6 (CH_3O), 121.3, 123.9, 128.4, 129.5, 130.1, 130.2, 135.0 and 149.4 (NPh and CPh) and 170.9 (C=O).

1,2-Diphenylaziridine. A solution of 1.0 M tetra-*n*-butylammonium fluoride (2.0 ml, 1.97 mmol) in THF was added dropwise to a stirred solution of *trans*-1,3-diphenyl-2-trimethylsilylaziridine (0.48 g, 1.79 mmol) in acetonitrile (3 ml) under nitrogen. The orange–brown solution was heated under reflux at 70 °C (18 h). The reaction mixture was quenched with distilled water (4 ml), extracted with diethyl ether (2 × 10 ml) and dried over anhydrous magnesium sulfate. The ethereal solution was concentrated to dryness to afford impure red–brown liquid l,2-diphenylaziridine (0.24 g, 69.2%). The product was confirmed by comparison of spectra with those of an authentic sample.[32]

2-Methoxycarbonyl-1-phenylaziridine. This product was obtained under various conditions when 2-methoxycarbonyl-1-phenyl-2-triethylsilylaziridine or 2-methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine was reacted with tetrabutylammonium fluoride or caesium fluoride in the presence and absence of other reagents such as silica gel or 18-crown-6. Isolation of the product was carried out in the following manner. The reaction mixture was diluted with ether and the solution washed with several portions of brine, in order to remove the fluoride source. The resultant solution was then dried and evaporated prior to purification by column chromatography on silica, using hexane or pentane as the eluent. Pure aziridine was recovered in the later fractions; ν_{max} (neat)/cm^{-1} 3090–2835, 1745, 1595, 1490, 1300–1250, 1200, 1120, 1195, 1005, 910, 840, 795 and 700; δ_H (400 MHz, $CDCl_3$, Me_4Si) 2.26 (1H, dd, *J* 1.46 and 6.34, $CHCO_2Me$), 2.63 (1H, dd, *J* 1.46 and 2.91, NCH_aH_b), 2.76 (1H, dd, *J* 6.34 and 2.91, NCH_aH_b), 3.74 (OCH_3), 6.88–7.55 (5H, m, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) 33.7 (CH_2), 37.5 (CH), 52.1 (OCH_3), 120.7, 123.4, 129.1 and 152.5 (Ph) and 170.5 (C=O).

Dried tetrabutylammonium fluoride. This method was used to dry samples of commercial 1 M tetrabutylammonium fluoride in THF containing 5 wt% water. A 10 cm^3 teflon sealed vial was partially filled with 4 Å molecular sieves which had been dried by heating for 1 day in an oven at 200 °C and then in a vacuum oven at 90 °C for three days. The vial was then filled with the tetrabutylammonium fluoride solution. After several hours of shaking the liquid was quickly transferred into a second vial containing fresh, activated molecular sieves and shaken for 24 hours. The preparation was used within the next 24 hours. When used, the material was removed by syringe and transferred to the reaction vial.

2-Methoxycarbonyl-2-deutero-1-phenylaziridine. 2-Methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine (0.05 g, 0.161 mmol) was placed in a 5 mm NMR tube with 0.5 ml dry deuterochloroform under nitrogen. Dried acetone (0.023 ml, 0.318 mmol) was introduced by syringe and the tube shaken to mix the reagents. A volume of dried tetrabutylammonium fluoride corresponding to 0.1 mol equivalents was then added. NMR spectroscopy indicated immediate and complete conversion to 2-methoxycarbonyl-2-deutero-1-phenylaziridine. The sample was taken up in ether, washed with brine, dried, evaporated and purified by column chromatography on silica, using pentane as the eluent; δ_H (400 MHz, $CDCl_3$, Me_4Si) 2.24 (1H, s, CH_aH_b), 2.60 (1H, s, CH_aH_b), 3.76 (3H, s, OCH_3), 6.79–7.55 (5H, m, Ph); δ_C (100 MHz, $CDCl_3$, Me_4Si) 34.4 (CH_2), 38.1 (CD), 53.1 (OCH_3), 121.6, 124.0, 129.5 and 152.5 (Ph) and 170.1 (C=O) (Found M^+, 178.0731 (EI), $C_{10}H_{10}DNO_2$ requires M_r 178.0853).

2-Methoxycarbonyl-1-phenyl-2-(1-dimethylphenylsiloxyhexyl)aziridine. 2-Methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine (0.3 g, 0.965 mmol) was placed in a 2 ml Teflon sealed vial which had been dried by heating. Freshly distilled hexanal (0.17 ml, 1.447 mmol) was injected into the vial. The resultant mixture was then warmed and agitated, in order to ensure thorough mixing, and then cooled to −78 °C. Dry tetrabutylammonium fluoride (3 drops, *ca.* 5%) was added to the vial over a 5 minute period resulting in the formation of a yellow mixture. This was allowed to warm to 0 °C and then 0.5 ml dry THF was added. After a further 17 hours at this temperature the mixture was diluted with ether, washed well with brine, dried and evaporated to give mostly the fully desilylated material and the silylether adduct (2-methoxycarbonyl-1-phenyl-2-(1-dimethylphenylsiloxyhexyl)aziridine) as a minor product, along with some of the free alcohol and polymerized aldehyde. The product mixture was purified by column chromatography on silica, using pentane as the eluent to give the product silylether as a colourless viscous oil (0.020 g, 0.0487 mmol, 5.0%). None of the free alcohol could be isolated from the column owing to decomposition. Proton NMR data show that the product is present as a mixture of diastereoisomers which are denoted here as x and y; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.313, 0.335, 0.339 and 0.358 (4 × 3H, 4 × s, Me_2Si), 0.78–0.82 (3H, 2 overlapping triplets, CH_2Me_x and CH_2Me_y), 1.20–1.66 (8H, m, $CH_2CH_2CH_2CH_2$), 2.28 and 2.57 (1H, 2 × d, *J* 1.6, H_{xa} and H_{xb}), 2.51 and 2.64 (1H, 2 × d, *J* 2.0, H_{ya} and H_{yb}), 3.18 and 3.28 (3H, 2 × s, OMe_y and OMe_x), 4.14 and 4.38 (1H, 2 × dd, J_{Ix} 5.8, J_{2x} 8.4, J_{1y} 3.2, J_{2y} 8.0, HCOSi) and 6.62–7.58 (10H, m, PhN and PhSi); δ_C (100 MHz, $CDCl_3$, Me_4Si) −0.6, −0.2 ($SiMe_2$), 14.7 (CH_3), 23.3 (CH_3CH_2), 26.3 ($CH_3CH_2CH_2$), 32.4 ($CH_3CH_2CH_2CH_2$), 34.1 ($SiOCHCH_2$), 35.2 (NCH_2), 51.2 (CH_3O), 52.3 (CCO_2Me) and 72.2 (COSi) (Found $M^+ - CH_3$, 396.2006 (EI), $C_{24}H_{33}NO_3Si$ requires $M^+ - CH_3$, 396.1995).

2-Methoxycarbonyl-1-phenyl-2-(1-dimethylphenylsiloxybenzyl)aziridine. 2-Methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine (0.2 g, 0.643 mmol) was placed in a 2 ml teflon sealed vial which had been dried by heating. Benzaldehyde (0.13 ml, 1.28 mmol) which had been washed with sodium sulfite and sodium bicarbonate solutions then dried and distilled, was

injected into the vial. The resultant mixture was then warmed in order to ensure thorough mixing and then cooled in an ice–salt bath. Dry tetrabutylammonium fluoride (2 drops, *ca.* 5%) was added resulting in the formation of a brown mixture. This was maintained at 0 °C for 15 minutes and then 0.5 ml dry THF was added. After a further 0.5 hours the mixture was diluted with ether washed well with brine, dried and concentrated to give again, a silylether adduct, as the major product (*ca.* 80% by NMR) along with some of the free alcohol and fully desilylated material. The product mixture was purified by column chromatography on silica using pentane as the eluent to give the product as a colourless viscous oil (0.150 g, 0.360 mmol, 56%). None of the free alcohol could be isolated from the column owing to decomposition. Again, preliminary investigations indicated that the product is stable to treatment with fluoride ion; δ_H (400 MHz, $CDCl_3$, Me_4Si) 0.29 and 0.32 (2 × 3H, 2 × s, Me_2Si), 2.49 and 2.73 (2H, 2 × s, H_2C_x and H_2C_y), 3.28 and 3.31 (3H, 2 × s, OMe_x and OMe_y), 5.34 and 5.60 (1H, 2 × s, $PhCH_x$ and $PhCH_y$) and 6.64–7.91 (15H, m, NPh, CPh, SiPh); δ_C (400 MHz, $CDCl_3$, Me_4Si) −0.85, −0.33, −0.32, 1.7 (4 × CH_3, SiMe), 34.5 (H_2C_y), 34.7 (H_2C_x), 51.7, 51.8, 52.2 and 52.3 ($OMe_{x\&y}$ and $MeOCOC_{x\&y}$), 120.2–141.7 (14 resonances, NPh, CPh, SiPh), 150.2 and 150.7 (2 × *ipso* C from NPh), 168.7 and 169.1 ($MeOCO_{x\&y}$); *m*/*z* (EI) 417 (M^+, 16.3%), 402 (M^+ − Me, 7.4), 241, (PhC(H)OSiMe_2Ph, 46.8), 167 (32.9), 135 ($SiMe_2Ph$, 100.0), 77 (18.5) (Found: C, 71.5; H, 6.5; N, 2.9%. $C_{25}H_{27}NO_3Si$ requires: C, 71.9; H, 6.5; N, 3.3%).

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