# The synthesis of 2-trialkylsilylaziridines from vinyltrialkylsilanes or the reaction of α-chloro-α-silyl carbanions with imines

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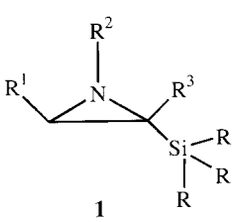
Three methods have been employed in the synthesis of 2-trialkylsilylaziridines. Firstly, reacting α-chloro-α-silyl carbanions with imines. Secondly, from the corresponding vinylsilane, *via* addition of bromoazide to give the 1-bromo-2-azide, followed by reduction. Finally, by the addition of organoazides to vinylsilanes using thermochemical and photochemical conditions. Using these three strategies a range of substitution patterns have been achieved.

## Introduction

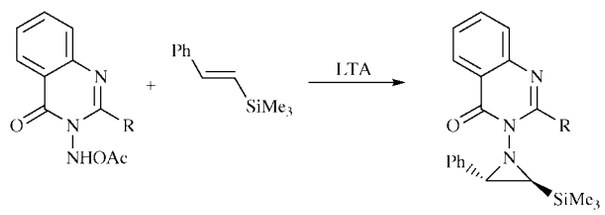
2-Trialkylsilylepoxides are important synthetic intermediates undergoing regiospecific and stereospecific transformations to give vinyl halides,[1] enol ethers[2] and carbonyl compounds.[3] Although much is known of the chemistry of 2-trialkylsilylepoexides, little is known of their 2-trialkylsilylaziridine counterparts. We were interested in investigating the synthetic versatility of these corresponding 2-trialkylsilylaziridines and in particular their ring opening reactions with electrophilic and nucleophilic reagents. To achieve this, it was necessary to synthesise 2-trialkylsilylaziridines, **1**, with a range of substituents, including hydrogen, on the ring nitrogen and ring carbons.




**1**

The first silicon containing aziridines were synthesised in 1964 by Adrianov *et al.*[4] by the thermal reaction of arylazides with vinylsilanes. This provides an effective route to 1-aryl-2-trialkylsilylaziridines,[5] but cannot be used to produce the corresponding 1-alkylaziridines. Zanirato and co-workers have used a similar methodology to prepare *N*-heteroaryltrimethylsilylaziridines.[6] With these thermochemical reactions the azide undergoes a 1,3-dipolar cycloaddition with the vinylsilane to give the intermediate triazolines which then lose nitrogen to give the corresponding 2-trialkylsilylaziridine. Addition of nitrenes to alkenes has also been used extensively to make aziridines. Lukevics *et al.* have generated nitrenes by α-elimination of carbamates and reacted them with vinylsilanes to produce 1-ethoxycarbonyl-2-trialkylsilylaziridines.[7] Atkinson and co-workers have developed a high yielding and stereoselective route to 2-trialkylsilylaziridines *via* a nitrene-like intermediate.[8] Reaction of acetoxyaminoquinazolone with lead tetraacetate (LTA) in the presence of alkenes leads to aziridines in good yield, as shown in Scheme 1. The introduction of a chiral centre at the 2 position of the quinazoline ring leads to asymmetric induction in the aziridination of prochiral trialkylsilylalkenes giving a ratio of diastereoisomers of 11 : 1.

2-Trialkylsilylaziridines have also been produced from alkenes *via* the formation of 1-halo-2-amines.[9–11] The stereochemistry of the product is determined by that of the 1-halo-2-amine which in turn is controlled by the manner in which the reagent adds to the alkene.




**Scheme 1**

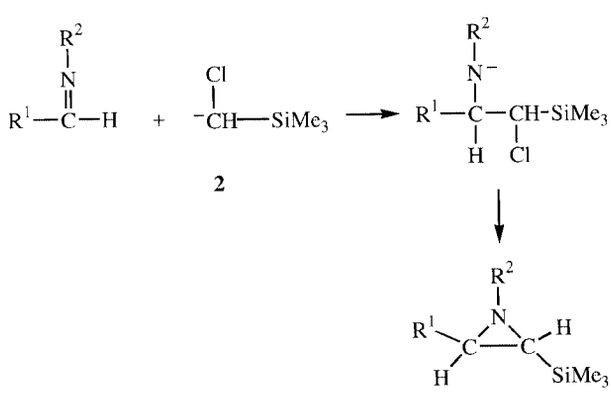
Despite the various 2-trialkylsilylaziridines that have been made, it was necessary to reexamine existing methodologies and develop new strategies, in order to generate a wide range of 2-trialkylsilylaziridines and hence enable us to examine methodically the effect of structure on the reactivity of these species.

## Results and discussion

### The synthesis of silylaziridines from imines

Cooke and Magnus have devised a route to α,β-epoxysilanes based on the reaction of a carbonyl compound with the α-silyl carbanion derived from α-chloromethyltrimethylsilane.[12] We have developed this reaction further to give silylaziridines from the corresponding azomethines, as shown in Scheme 2.

In a typical procedure the α-silyl carbanion, **2**, was formed by the reaction of α-chloromethyltrimethylsilane in freshly distilled tetrahydrofuran with a solution of *sec*-butyllithium–TMEDA in cyclohexane at −78 °C. The resultant carbanion was treated with a solution of an azomethine in tetrahydrofuran at about −65 °C. The mixture was allowed to stand for two hours at −50 °C, then quenched with aqueous ammonium chloride at room temperature and worked up as




**2**

**Scheme 2**

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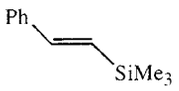
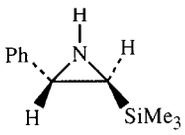
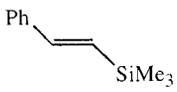
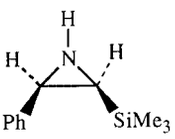
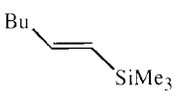
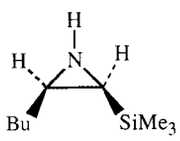
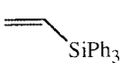
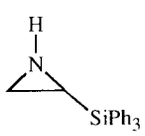
**Table 1** Yields of 2-trimethylsilylaziridines obtained *via* bromoazide addition

| Alkene | Procedure | Reducing agent | | Aziridine | Overall yield (%) |
|---|---|---|---|---|---|
|  | B | $LiAlH_4$ | **3** |  | 33 |
|  | A | $LiAlH_4$ | **4** |  | 66 |
|  | B | $PPh_3$ | **5** |  | 54 |
|  | A | $LiAlH_4$ | **6** |  | 51 |

normal. *N*-Benzylidenepropylamine gave stereoselectively the *cis*-1-propyl-2-trimethylsilyl-3-phenylaziridine in 53% yield. *N*-Benzylideneaniline gave the corresponding aziridine in 77% yield. However, rather than isolating only the *cis* compound a 1 : 1 mixture of *cis*- and *trans*-isomers was obtained which could be separated using column chromatography although the *E*-isomer did undergo some decomposition on the column.

Extension of this reaction to azomethines from ketones was unsuccessful, as has been reported for the corresponding epoxide synthesis of Cooke and Magnus. Reaction of the α-silyl carbanion with *N*-(1-phenylethylidene)propylamine gave no aziridine, but 1-phenyl-3-trimethylsilylpropan-1-one in 30% yield. This β-trimethylsilyl ketone was presumably obtained *via* deprotonation of the azomethine methyl group to give a metalloenamine which undergoes alkylation by the α-chloromethyltrimethylsilane. Unfortunately *N*-alkylidenealkylamines also failed to give aziridines by this route. The NMR spectrum of the reaction mixture obtained with *N*-hexylidenepropylamine again suggested metalloenamine formation rather than addition of the carbanion.

### Synthesis of silylaziridines *via* the addition of bromoazide to vinylsilanes

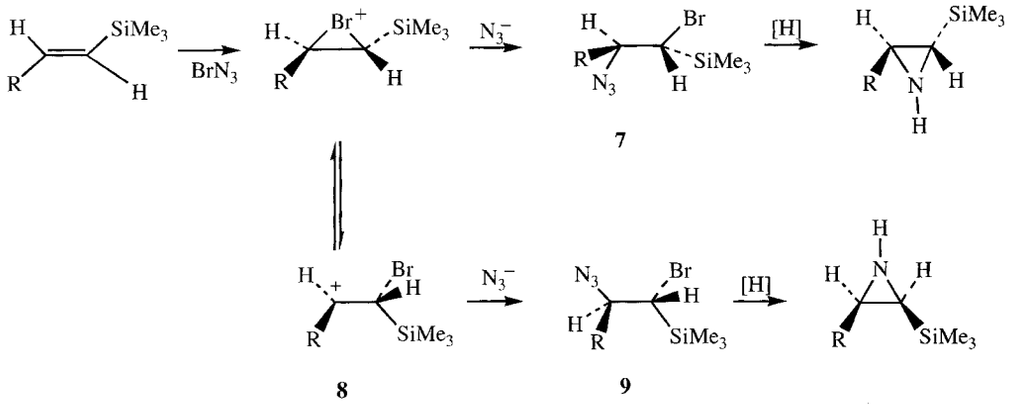
To provide a route to *N*-unsubstituted silylaziridines we examined the reaction between bromoazide and vinylsilanes. Duboudin and Laporte first used this route[11] and we have been able to extend it to provide a wider range of compounds. In particular we found that by altering the conditions it was possible to make either the *cis*- or *trans*-aziridine from the same alkene. The results are shown in Table 1. Starting with (*E*)-2-trimethylsilyl-1-phenylethene we have been able to obtain in good yields *cis*-2-trimethylsilyl-2-phenylaziridine using bromoazide prepared *in situ* from bromine and sodium azide in a mixture of dichloromethane and aqueous hydrochloric acid (Procedure A). The corresponding *trans*-2-trimethylsilyl-1-phenylaziridine is produced using *N*-bromosuccinimide and sodium azide in aqueous 1,4-dioxane (Procedure B). The stereochemistry of the aziridines was determined from their characteristic ring proton coupling constants.

Addition/elimination reactions of vinylsilanes can proceed with either retention or inversion depending upon the conditions and substrate structure.[13] This difference of behaviour is usually explained in terms of a nucleophilic attack of the bromonium ion or stereospecific nucleophilic attack on the carbocation resulting from ring opening. Applying these arguments to our system suggests that the first step involves formation of an intermediate bromonium ion, as shown in Scheme 3 (together with the corresponding enantiomer).[14]

Nucleophilic ring opening in a Markownikov fashion, that is β to silicon and α to phenyl, gives the *RR* and *SS* product, **7**. Reduction of the azide function to an amine using lithium aluminium hydride, followed by ring closure, then gives the *trans*-aziridine. The *cis*-aziridine is formed *via* reduction and cyclisation, from the (*RS*)- and (*SR*)-bromoazide, **9**. This is formed from attack of the azide ion, not on the cyclic bromonium ion, but on the free carbocation, **8**. Ring opening of the bromonium ion followed by least motion rotation, so that the carbon–silicon bond is in line with the empty p orbital, gives **8**. This is then attacked by the azide ion from the least hindered side, that opposite the bulky trimethylsilyl group, to give the (*RS*)- and (*SR*)-bromoazide.

If such a rationale applies to the change in stereochemistry observed in our system, it implies that nucleophilic attack occurs on a bromonium ion with bromoazide formed from *N*-bromosuccinimide in 1,4-dioxane and on an open chain carbocation species with bromoazide formed from bromine in dichloromethane. Why a particular intermediate predominates under one set of conditions is hard to understand and would require a detailed analysis of the reaction mixtures from a wide range of vinylsilanes, including the *Z*-isomers. Nevertheless, the literature suggests that such a change is by no means without precedent. For example, Chan and Kaumaglo observed a similar change in stereochemistry on addition of a Lewis acid in their 'tuneable' stereoselective alkene synthesis based on iodosilylation of vinylsilanes.[15] Interestingly, the other alkenes which were examined gave exclusively the *trans*-aziridines, arising from bromonium ion formation, irrespective of the conditions employed. In these cases there was not an adjacent phenyl group to stabilise the open chain carbocation so the alternative route was not viable.

Reduction of the 1-bromo-2-azide to the 1-bromo-2-amine followed by cyclisation did not always occur readily with lithium aluminium hydride. In particular, 2-azido-1-bromo-1-trimethylsilylhexane proved difficult to reduce. Lithium aluminium hydride reduced the 1-bromo-2-azide to 2-amino-1-

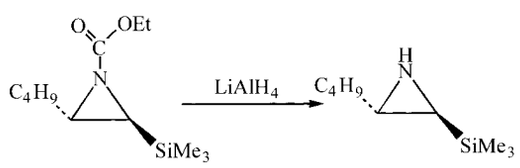


**Scheme 3**

trimethylsilylhexane. K-Selectride led to the aziridine, but it was difficult to remove the tri-*sec*-butylboron group which became attached to the aziridine nitrogen. A range of hydrogenation catalysts and solvents were examined, but in general the outcome was the elimination of trimethylsilyl azide. For this substrate the most effective reagent was triphenylphosphine. Presumably an intermediate *N*-(triphenylphosphonio)aziridine is formed which is then hydrolysed to triphenylphosphine oxide and the free aziridine.

### Synthesis of silylaziridines by the reaction of organoazides with vinylsilanes

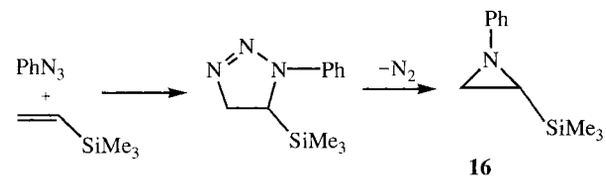
The addition of an organoazide to an alkene has been used extensively to make aziridines and the method has been applied to the synthesis of 1-trimethylsilylaziridines. The reaction can occur both photochemically or thermally. Photochemical addition of organoazides is thought to involve formation of a nitrene. Table 2 gives the range of 2-trimethylsilylaziridines we have prepared photochemically. The reactions were carried out in the absence of solvent and were generally complete within two to four days. In all cases retention of the configuration was observed, suggesting reaction *via* the singlet nitrene.[16] The 1-ethoxycarbonyl-2-trimethylsilylaziridines can be further functionalised to give other 2-trimethylsilylaziridines. For example, reduction with lithium aluminium hydride does not lead to ring opening but to loss of the ethoxycarbonyl group to give the NH aziridine, as shown in Scheme 4. This has provided an alternative route to *trans*-3-butyl-2-trimethylsilylaziridine.



**Scheme 4**

Organoazides may also generate nitrenes by a thermal reaction, however, we have observed that this thermal decomposition often occurs at temperatures greater than is required for the thermal addition of phenyl azide to alkenes, which has been shown to give the corresponding aziridine *via* the triazoline, as shown in Scheme 5.[5,6]

We re-examined the addition of phenyl azide and found that with trimethylsilylethene the highest yield was obtained when no solvent was employed. As shown in Tables 2 and 3, the thermal route to 1-phenyl-2-trimethylsilylaziridine leads to a higher yield than the photochemical route. If the reactions involving trimethylvinylsilane were stopped part way through, it was found that most of the reactant had disappeared and the solution contained mainly the intermediate triazoline. However, the intermediate triazoline could not be observed with the other



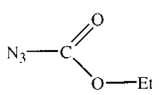
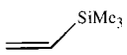
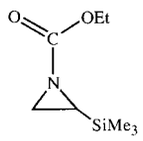
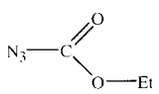
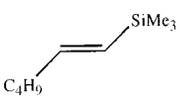
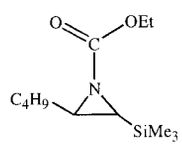
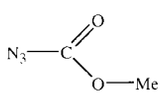
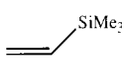
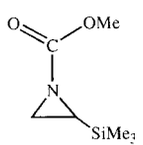
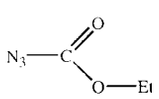
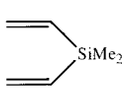
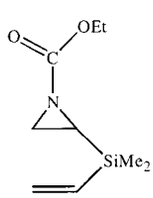
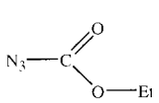
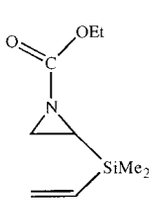
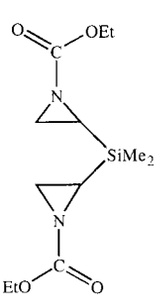
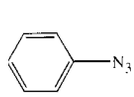
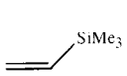
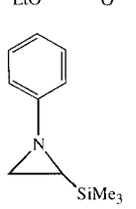
**Scheme 5**

vinylsilanes. Presumably, the presence of the ester group on the ring carbon facilitated the loss of nitrogen. In none of the cases was any enamine detected, as has been reported elsewhere.[5]

Methyl 2-triethylsilylpropenoate was prepared by the hydrosilylation of methyl propynoate. The literature reports chloroplatinic acid can be used to give a 70% yield of the product with 30% of the vicinal regioisomer.[17] We found that with this catalyst 70% of the vicinal isomer was obtained and only 30% of the desired compound. However, use of 10% platinum on carbon gave 70% of the geminal regioisomer. The two isomers could be separated by column chromatography, but in most cases a partially purified mixture of regioisomers was used since addition of the phenyl azides only takes place with the geminal compound. Hydrosilylation with dimethylphenylsilane and platinum on carbon again gave mainly the geminal isomer, which again reacts selectively with phenyl azide. However, whilst reaction of methyl propynoate with diphenylmethylsilane gave predominantly the geminal isomer, in this case both regioisomers underwent addition with phenyl azide, such that isolation of the required aziridine was not possible.

Our initial objective for this work was to devise routes to 2-trialkylsilylaziridines, **1**, with a range of substituents, including hydrogen, on the ring nitrogen and carbons. The various approaches outlined in this paper provide routes to most of the possible aziridine types. 1-Alkyl-2-trialkylsilylaziridines are best prepared by reaction of an α-chloro-α-silyl carbanion with an imine. Whilst 1-alkyl-3-aryl-2-trialkylsilylaziridines are readily obtained, the corresponding 3-alkyl or disubstituted compounds could not be prepared. A possible alternative route to this type of compound is *via* the cyclic sulfate.[18] These are prepared by dihydroxylation of the alkene followed by treatment with thionyl chloride and $NaIO_4$–$RuCl_3$.[19] Reaction with an appropriate amine, followed by treatment with butyllithium leads to the corresponding aziridine. However, we have found that this route is limited by the stability of the 1-trialkylsilyl cyclic sulfate to the reaction conditions for its preparation and we have been unable to extend it to alkyl substituted alkenes. An alternative method of preparing the cyclic sulfate is *via* reaction of phenyl iodosulfate with the vinylsilane and we shall be investigating this route to 2-trimethylsilylaziridines in the future.[20] 1-Aryl-2-trialkylsilylaziridines are best prepared by the addition of aryl or heteroaryl azides to vinylsilanes *via* a thermal route. They can also be formed by reaction of an α-chloro-α-silyl carbanion with an *N*-arylimine. Aziridines con-

**Table 2** Yields of 2-trimethylsilylaziridines prepared by the photochemical addition of organoazides to vinylsilanes

| Organoazide | Alkene | Aziridine | | Yield (%) |
|---|---|---|---|---|
|  |  |  | **10** | 64 |
|  |  |  | **11** | 60 |
|  |  |  | **12** | 25 |
|  |  |  | **13** | 53 |
|  |  |  | **14** | 29 |
|  |  |  | **15** | 50 |

taining an electron withdrawing group attached to the nitrogen can be prepared *via* photolysis of the corresponding organoazide. 2-Trialkylsilylaziridines without a substituent on the nitrogen can be formed *via* a number of routes. Addition of bromoazide to the alkene gives the 1-bromo-2-azide which can be reduced to the alkene, however, we have found this latter stage to be temperamental. An alternative route is *via* reduction of the *N*-alkoxycarbonylaziridine, which is prepared by photolysis of the alkyl azidoformates in the presence of the vinylsilane.

In conclusion we have found that the synthesis of 2-trialkylsilylaziridines, **1**, cannot be achieved by any one method but requires a number of strategies to obtain the required range of substitution patterns.

## Experimental

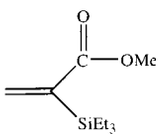
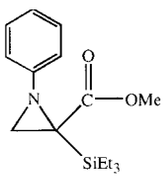
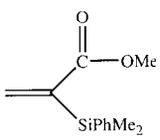
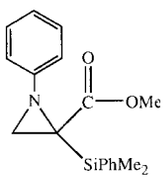
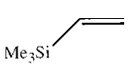
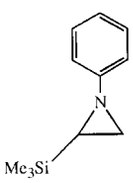
Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. Infrared spectra were obtained as Nujol mulls or thin films using sodium chloride plates or as KBr discs on a Pye Unicam SP1050 or a Nicolet 205 FT-IR spectrometer. NMR spectra were recorded as solutions in deuteriochloroform 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.

### The synthesis of aziridines using α-chloromethyltrimethylsilane and azomethines

These reactions were carried out according to the general procedure described below.

***cis*-3-Phenyl-1-propyl-2-trimethylsilylaziridine.** Typically, a solution of *sec*-butyllithium (1.42 g, 22.20 mmol) was added to a solution of α-chloromethyltrimethylsilane (2.50 g, 20.40 mmol) and TMEDA (2.37 g, 20.40 mmol) in THF under nitrogen at −78 °C. The yellow–orange solution was stirred at −78 °C (1 h) and the temperature of the cold bath raised to *ca.* −65 °C. To this was added a solution of *N*-benzylidenepropylamine (3.00 g, 20.40 mmol) in THF (3 ml). The temperature was raised to *ca.* −40 °C and the resultant orange solution was stirred (1 h). The bath temperature was finally raised to room temperature. The reaction mixture was stirred over 17 h under nitrogen to give a deep reddish orange solution. This was quenched with a saturated solution of ammonium chloride (20

**Table 3** Yields of trimethylsilylaziridines prepared by the thermal addition of phenyl azide to vinylsilanes

| Alkene | Aziridine | Yield (%) | |
|---|---|---|---|
|  |  | **16** | 70 |
|  |  | **17** | 88 |
|  |  | **15** | 61 |

ml), followed by extraction with diethyl ether (3 × 20 ml) and the yellow organic layer was dried over anhydrous magnesium sulfate. The filtrate was concentrated at 40 °C/15 mmHg and was distilled under reduced pressure to give *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine (2.5 g, 53%), bp 46–48 °C/0.02 mmHg; $\nu_{max}$(neat)/cm$^{-1}$ 3000, 2850, 1250, 850 and 700; $\delta_H$(90 MHz, $CDCl_3$, $Me_4Si$) −0.23 (9H, s, $SiMe_3$), 0.10 (1H, d, *J* 7.5, CH), 1.00 (3H, t, $CH_2$-C$H_3$), 1.70 (2H, m, $CH_2$-C$H_2$-$CH_3$), 2.60 (1H, d, *J* 7.5, CH), 3.6 (2H, t, N-$CH_2$) and 6.80 (5H, m, Ph); $\delta_C$(22.5 MHz, $CDCl_3$, $Me_4Si$) −1.84 ($SiMe_3$), 12.04 ($CH_2$-*C*$H_3$), 23.41 ($CH_2CH_2CH_3$), 38.14 (*C*-$SiMe_3$), 46.36 (*C*Ph), 66.32 (N-*C*$H_2$), 126.36, 127.79, 128.60 and 140.26 (Ph) (Found: C, 72.1; H, 10.0; N, 6.1. $C_{14}H_{23}N$ requires C, 72.0; H, 9.9; N, 6.0%).

***cis* and *trans*-1,3-Diphenyl-2-trimethylsilylaziridines.** The reaction was carried out using *sec*-butyllithium (0.86 g, 13.50 mmol), chloromethyltrimethylsilane (1.50 g, 12.20 mmol), TMEDA (1.42 g, 12.20 mmol) and *N*-benzylideneaniline (2.21 g, 12.20 mmol). A sample of the reaction mixture was separated by chromatography on a silica column using diethyl ether–hexane (1:11) to give *cis*- and *trans*-1,3-diphenyl-2-trimethylsilylaziridines in the ratio of 52:48 (2.52 g, overall yield 77.1%).

***cis*-1,3-Diphenyl-2-trimethylsilylaziridine.** 1.30 g; $\nu_{max}$(neat)/cm$^{-1}$ 3150, 2850, 1600, 1500, 1410, 1260, 850, 750 and 690; $\delta_H$(90 MHz, $CDCl_3$, $Me_4Si$) −0.12 (9H, s, $SiMe_3$), 1.70 (1H, d, *J* 8.0, CH), 3.45 (1H, d, *J* 8.0, CH) and 6.95–7.65 (10H, m, 2 × Ph); $\delta_C$(22.5 MHz, $CDCl_3$, $Me_4Si$) −1.95 ($SiMe_3$), 38.37 (*C*-$SiMe_3$), 46.07, 120.35, 122.25, 127.01, 127.59, 128.05, 129.91, 139.25 and 157.60 (2 × Ph) (Found: C, 76.2; H, 7.7; N, 5.2. $C_{17}H_{21}NSi$ requires C, 76.3; H, 7.9; N, 5.2%).

***trans*-1,3-Diphenyl-2-trimethylsilylaziridine.** Was obtained as white crystals (1.22 g); $\nu_{max}$(Nujol)/cm$^{-1}$ 3063, 3033, 2954, 2923, 2856, 1702, 1598, 1492, 1456, 1401, 1318, 1253, 1218, 1178, 1146, 1095, 1969, 1026, 999, 932, 896, 844, 792, 760, 717, 697 and 669; $\delta_H$(90 MHz, $CDCl_3$, $Me_4Si$) −0.04 (9H, s, $SiMe_3$), 1.85 (1H, d, *J* 4.5, CH), 3.28 (1H, d, *J* 4.5, CH) and 6.85–7.48 (m, 10H, 2 × Ph); $\delta_C$(22.5 MHz, $CDCl_3$, $Me_4Si$) −2.01 ($SiMe_3$), 41.30 (*C*-$SiMe_3$), 42.85 (*C*-Ph), 120.80, 121.90, 126.50, 127.10, 128.30, 128.70, 139.50 and 152.20 (2 × Ph) (Found: C, 76.1; H, 7.8; N, 5.1. $C_{17}H_{21}NSi$ requires C, 76.3; H, 7.9; N, 5.2%).

**1-Phenyl-3-trimethylsilylpropan-1-one.** The reaction was carried out using *sec*-butyllithium (2.19 g, 34.20 mmol), chloromethyltrimethylsilane (3.8 g, 31.06 mmol), TMEDA (3.61 g, 30.98 mmol) and *N*-(methylbenzylidene)propylamine (5.00 g, 31.20 mmol). The reaction mixture was analysed by TLC and GLC. The chromatogram showed recovery of the starting azomethine (65.9%). Three other components at higher retention times were detected in the following respective yields: 1.5, 4.0 and 28.6% w/w. The reaction was further purified on a silica column using hexane–diethyl ether as eluent (11:1). The azomethine decomposed to give acetophenone (60%). 1-Phenyl-3-trimethylsilylpropan-1-one was obtained (30%) and characterised by $^1$H NMR, $\delta_H$(90 MHz, $CDCl_3$, $Me_4Si$) 0.00 (9H, s, $SiMe_3$), 0.82 (2H, t, *J* 9.0, Si-$CH_2$), 2.85 (2H, t, *J* 9.0, $CH_2$-CO) and 7.32–8.10 (5H, m, Ph). The product was confirmed by comparison with the spectrum of an authentic sample.[21]

### The synthesis of 1-bromo-2-azides *via* the addition of bromoazide to vinylsilanes (Procedure A)

With the modifications given below, the following general method, which is similar to that used by Duboudin and Laporte,[11] was applied to the synthesis of bromoazides from *trans*-trimethylsilylstyrene and triphenylvinylsilane. The method is described for *trans*-trimethylsilylstyrene.

**(*RS*)/(*SR*)-2-Azido-1-bromo-2-phenyl-1-trimethylsilylethane.** Bromine (8.00 g 50 mmol) was added dropwise to an ice-cooled mixture of sodium azide (32.5 g 500 mmol) in 100 ml of dichloromethane containing 25 ml of 30% hydrochloric acid. The mixture was stirred for 45 minutes. The organic layer containing the bromoazide was decanted from the aqueous layer and suspended solids, and added dropwise to a stirring, precooled (−5 °C) solution of *trans*-trimethylsilylstyrene (8.80 g 50 mmol) in dichloromethane. The mixture was stirred for 45 minutes at 0 °C. Washing with two 50 ml portions of dilute sodium bicarbonate solution was followed by rotary evaporation at room temperature to give (*RS*)/(*SR*)-2-azido-1-bromo-2-phenyl-1-trimethylsilylethane as a pale pink oil, (12.5 g, 42 mmol, 84%). This was contaminated by a small amount (*ca.* 5% by NMR spectroscopy) of the *SS*/*RR* adduct. Column chromatography failed to separate these isomers and so the product was used in the next step as a mixture; $\nu_{max}$(neat)/cm$^{-1}$ 2100(str), 1490, 1450, 1310, 1430, 1240, 740 and 700; $\delta_H$(90 MHz, $CDCl_3$, $Me_4Si$) 0.09 (9H, s, $SiMe_3$), 3.68 (1H, d, *J* 9.03, CBr), 4.84 (1H, d, *J* 9.03, $CN_3$) and 7.42 (5H, s, Ph); $\delta_C$(90 MHz, $CDCl_3$, $Me_4Si$) −1.55 ($SiMe_3$), 47.45 (CSi), 6.91 (CPh), 127.93, 129.48, 129.66 and 129.37 (Ph).

**2-Azido-1-bromo-1-triphenylsilylethane.** In a modification of the general procedure A, this azide was prepared using an increased proportion of sodium azide to bromine, in order to preclude formation of the dibromo adduct. Also, the product mixture was stirred at room temperature for an additional 7 hours prior to work up to ensure complete reaction. The reaction was carried out using; vinyltriphenylsilane (7.5 g, 26 mmol), bromine (4.8 ml, 30 mmol), sodium azide (30 g, 462 mmol) and 20% hydrochloric acid (20 ml). Evaporation of the organic layer yielded a pale orange solid. Recrystallization from a mixture of chloroform–hexane (2:5) gave 2-azido-1-bromo-1-triphenylsilylethane as a white solid (6.85 g, 16.8 mmol, 56%); $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 3.36 (1H, dd, *J* 10.4, 13.6, HCBr), 3.89 (1H, dd, *J* 2.8, 13.6, $H_aH_bCN_3$), 4.10 (1H, dd, *J* 2.8, 10.4, $H_aH_bCN_3$), 7.46–7.69 and 7.75–7.95 (15H, m, 3 × Ph); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) 37.0 (CSi), 54.8 ($CN_3$), 127.6, 130.1, 131.2 and 135.8 (3 × Ph).

### The synthesis of 1-bromo-2-azides *via* the addition of bromoazide to vinylsilanes (Method B)

This method was used to prepare the corresponding bromoazides from *trans*-trimethylsilylstyrene and *trans*-1-tri-

methylsilylhex-1-ene. The method is described for *trans*-trimethylsilylstyrene.

**(*SS*)/(*RR*)-2-Azido-1-bromo-2-phenyl-1-trimethylsilylethane.** *N*-Bromosuccinimide (24 g, 135 mmol) was added in small portions to a pre-cooled (−6 °C), stirred mixture of aqueous (100 ml) sodium azide (22.3 g, 343 mmol) in 1,4-dioxane (300 ml) containing the alkene *trans*-trimethylsilylstyrene (16.9 g, 96.2 mmol). The mixture was then stirred at 0 °C until the orange colour of the bromoazide disappeared (30 min–1 h) and a clear solution remained. This was washed several times with brine and extracted with ether. Following concentration, residual succinic acid was removed by precipitation in carbon tetrachloride. The product oil, (*SS*)/(*RR*)-2-azido-1-bromo-2-phenyl-1-(trimethylsilyl)ethane was recovered as a single diastereoisomer and purified by flash column chromatography on silica using neat hexane as the eluent (20.6 g, 69.1 mmol, 72%); $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$), 0.24 (9H, s, $Me_3Si$), 3.64 (1H, d, *J* 8.4, CHBr), 4.84 (1H, d, *J* 8.4, $CHN_3$) and 7.32 (5H, s, Ph).

**2-Azido-1-bromo-1-trimethylsilylhexane.** This was prepared in 71% yield, as a colourless oil by the general procedure B using: *N*-bromosuccinimide (24.0 g, 135 mmol), sodium azide (22.3 g, 343 mmol) and *trans*-1-trimethylsilylhex-1-ene (15.5 g, 96.2 mmol); $\nu_{max}$(neat)/$cm^{-1}$ 2960, 2100, 1250 and 840; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$), 0.21 (9H, s, $Me_3Si$), 0.80–1.05 (3H, m, $CH_3$), 1.10–2.80 (6H, m, $CH_2CH_2CH_2$), 3.39 (1H, d, *J* 5.1, CHBr) and 3.49–3.95 (1H, m, $CHN_3$); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) 0.574 ($SiMe_3$), 14.4 ($CH_3$), 24.59 ($CH_2CH_3$), 30.79 ($CH_2CH_2CH_3$), 35.44 ($CH_2CHN$), 47.80 (CSi) and 67.73 (CN) (Found: C, 39.0; H, 7.5. $C_9H_{20}N_3BrSi$ requires C, 38.8; H, 7.2%).

### The synthesis of trimethylsilylaziridines by reduction of 1-bromo-2-azides with lithium aluminium hydride

Lithium aluminium hydride reduction of the corresponding 1-bromo-2-azide was used to form *cis*-3-phenyl-2-trimethylsilylaziridine, *trans*-3-phenyl-2-trimethylsilylaziridine and 2-triphenylsilylaziridine. The method is described for preparation of *cis*-3-phenyl-2-trimethylsilylaziridine.

***cis*-3-Phenyl-2-trimethylsilylaziridine, 4.** A slurry of lithium aluminium hydride (1.7 g, 44.8 mmol) in dry ether (30 ml) was cooled (ice-salt bath) with stirring under nitrogen. (*RS*)/(*SR*)-2-Azido-1-bromo-2-phenyl-1-trimethylsilylethane (95%, 4.61 g, 14.7 mmol) in dry ether (5 ml) was added dropwise over 10 min carefully maintaining the temperature below 0 °C. Slight effervescence was accompanied by the production of a pale olive green colour. The mixture was stirred for a further 45 minutes at 0 °C and then allowed to warm to room temperature. Stirring was continued for a further 17 hours. Recooling to 0 °C was followed by slow hydrolysis with 9 ml of a 20% sodium hydroxide solution, added dropwise with stirring over a period of 15 minutes. After warming to room temperature, the solution was stirred rapidly for 45 minutes. The resulting fine white granular solid was washed well with ether and the mother liquor and washings were carefully dried with magnesium sulfate over several hours. Concentration gave 2.6 g of a colourless, oily product. Purification of this by flash column chromatography on silica gel, using pentane as the eluant was accompanied by substantial decomposition giving 1.1 g (5.76 mmol, 39%) of *cis*-3-phenyl-2-trimethylsilylaziridine as a colourless, pungent smelling oil; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) −8.22 (9H, s, $SiMe_3$), 1.11 (1H, s, NH), 1.34 (1H, d, *J* 7.3, C*H*$SiMe_3$), 3.40 (1H, d, *J* 7.3, C*H*Ph) and 7.16–7.32 (5H, C's Ph); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) −2.12 ($SiMe_3$), 27.69 (C-Si), 37.11 (C-Ph), 126.50, 127.42, 127.65 and 139.42 (Ph); *m*/*z* (EI) 190 ($M^+ - H$, 26.8%), 176 ($M^+ - CH_3$, 5.8), 161 ($M^+ - 2 \times CH_3$, 161), 117 (10.5), 105 (40.5), 91 (16.9), 77 (23.3) and 73 ($SiMe_3$, 100).

***trans*-3-Phenyl-2-trimethylsilylaziridine, 3.**[6] This compound was prepared (91%) according to the procedure for *cis*-3-phenyl-2-trimethylsilylaziridine using (*RR*)/(*SS*)-2-azido-1-bromo-2-phenyl-1-trimethylsilylethane (3.6 g, 12.1 mmol) and lithium aluminium hydride (1.38 g, 36.3 mmol). The product was purified by column chromatography, on silica using hexane as the eluent; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 0.03 (9H, s, $SiMe_3$), 0.83 (1H, s, NH), 1.13 (1H, d, $J_{trans}$ 4, C*H*Ph), 2.80 (1H, d, *J* 4, C*H*Ph) and 7.21 (5H, s, Ph); $\delta_C$(400 MHz, $CDCl_3$, $Me_4Si$) −0.40 ($Me_3Si$), 32.28 (CHSi), 35.44 (CHPh), 126.15, 127.22, 128.2 and 141.20 (Ph).

**2-Triphenylsilyl aziridine 6.** This was prepared using 2-azido-1-bromo-1-triphenylsilylethane (3.0 g, 7.35 mmol) and lithium aluminium hydride (0.75 g, 19.8 mmol). The white solid that was obtained was recrystallised from 2:5 chloroform–hexane yielding 1.98 g, (6.58 mmol, 89.5%) 2-triphenylsilylaziridine as fine white plates, which decompose on heating; $\nu_{max}$(Nujol)/$cm^{-1}$ 3045, 2900, 1590, 1485, 1430, 1115, 855, 800, 730 and 700; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 1.42 (1H, d, *J* 7.2, $CH_aH_bCH_c$), 1.64 (1H, d, *J* 6.4, $CH_aH_bCH_c$), 1.88 (1H, d, *J* 6.8, $CH_aH_bCH_c$), 7.22–7.29 (10H, m, $Ph_3Si$) and 7.52–7.61 (5H, m, $Ph_3Si$); $\delta_C$(400 MHz, $CDCl_3$, $Me_4Si$), 15.23 (CSi), 22.02 (CN), 127.80, 129.48, 135.77 and 136.70 ($Ph_3Si$); *m*/*z* (EI) 301 ($M^+$, 8.2%), 259 ($SiPh_3$, 12.0), 182 ($SiPh_2$, 17.3), 180 (24.3), 105 (SiPh, 12.3), 94 ($PhN^+H_3$) and 73 (100.0) (Found: C, 79.4; H, 6.5. $C_{20}H_{19}NSi$ requires C, 79.7; H, 6.3%).

### The synthesis of *trans*-2-trimethylsilyl-3-butylaziridine 5 by reaction of 2-azido-1-bromo-1-trimethylsilylhexane with triphenylphosphine

To a solution of 2-azido-1-bromo-1-trimethylsilylhexane (0.28 g, 1.01 mmol) in THF (4 ml) was added triphenylphosphine (0.22 g, 1.10 mmol). The resulting yellow mixture was heated to 50 °C and stirred rapidly for 1.5 h. On cooling to room temperature, 5 ml of 2 M sodium hydroxide were added followed by stirring for 1 h. The mixture was extracted with ether, dried and concentrated. On addition of hexane a white solid precipitated, leaving a yellow oil. The oil was separated from the solid and purified by flash column chromatography to give *trans*-3-butyl-2-trimethylsilylaziridine as a colourless oil (0.13 g, 0.765 mmol, 76%); $\nu_{max}$(neat)/$cm^{-1}$ 3000–2850, 1710, 1455, 1245, 1100 and 870–820; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) −0.05 (9H, s, $Me_3Si$), 0.63 (1H, d, *J* 4.6, CHSi), 0.69–1.57 (9H, m, $CH_3CH_2$-$CH_2CH_2$) and 2.61–2.85 (1H, m, $NCH_2CH_2$); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) 3.27 ($Me_3Si$), 14.13 ($CH_3$), 22.69 ($CH_3CH_2$), 26.54 (CHSi), 30.16 ($CH_3CH_2CH_2$), 34.58 ($NCHCH_2$) and 37.521 ($NCHCH_2$); *m*/*z* (EI) 172 ($[M + H]^+$, 100.0%), 128 (5), 100 (12) and 98 ($M^+ - SiCH_3$, 6) (Found: $(M + H)^+$, 172.1524 (EI). $C_9H_{22}NSi$ requires *M* 172.1443).

### Synthesis of 2-trimethylsilylaziridines by the photochemical reaction of organoazides with vinylsilanes

**1-Ethoxycarbonyl-2-trimethylsilylaziridine, 10.**[7] Ethyl azidoformate (3.4 g, 30 mmol) and vinyltrimethylsilane (1.5 g, 15 mmol) were placed in a quartz tube and irradiated at 254 nm for 48 hours using a medium pressure arc carousel (rayonet). The tube was then recharged with vinyltrimethylsilane (1.5 g, 15 mmol) and irradiated for a further 48 hours. The resultant yellow oil was purified by chromatography on a silica-gel column, using ether–pentane (1:20) as the eluent. Fractions were collected and analysed by TLC. The pure aziridine (3.6 g, 19.3 mmol, 64%) was obtained in the first fraction as a sweet smelling colourless oil; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 0.07 (9H, s, $Me_3Si$), 1.27 (3H, t, *J* 7.2, $CH_3$), 1.65 (1H, dd, *J* 5.1, 7.3, SiCH), 2.04 (1H, dd, *J* 5.1, 1.2, $CH_aCH_b$), 2.38 (1H, dd, *J* 7.2, 1.2, $CH_aH_b$) and 4.13 (2H, q, *J* 7.2, $OCH_2$); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) 14.3 ($CH_2CH_3$), 28.1 (CHSi), 28.4 ($CH_2N$), 62.2 ($CH_2CH_3$) and 164.2 (C=O).

***trans*-3-Butyl-1-ethoxycarbonyl-2-trimethylsilylaziridine, 11.** *trans*-1-Trimethylsilylhex-l-ene (6.24 g, 40 mmol) was placed in

a quartz tube for irradiation. Ethyl azidoformate was added over eight days in four equal portions of 1.15 g (10 mmol), during the irradiation process. Hexane (10 ml) was added to the resultant yellow oil effecting precipitation of a white solid. The mixture was filtered and the mother liquor concentrated to give a pale yellow oil. This was purified by chromatography on silica gel, using hexane as the eluent. The fractions were analysed by NMR spectroscopy. Residual alkene was collected in the early fractions. Later fractions yielded the pure aziridine as a colourless, faintly sweet smelling oil (4.1 g, 24.0 mmol, 60%); $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 0.06 (9H, s, $Me_3Si$), 0.91 (3H, t, $CH_2$-$CH_2CH_3$), 0.77 (1H, d, *J* 6.3, C*H*Si), 1.12–1.53 (9H, m, $CH_2CH_2CH_2$ and $CH_3CH_2O$), 2.04–2.34 (1H, m, $CH_2CHN$) and 4.12 (2H, q, $OCH_2$); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) −2.9 ($Me_3Si$), 14.0 ($CH_3$), 14.4 ($CH_3$), 22.4 ($CH_3CH_2CH_2$), 29.4 ($CH_3CH_2CH_2$), 33.2 (NCH*C*H2), 35.2 (CHSi), 40.3 (*C*$HCH_2$), 61.9 ($CH_2O$) and 163.0 (C=O); *m*/*z* (EI) 244 ([M + H]$^+$, 13.7%), 228 ($M^+ - CH_3$, 26.6), 214 ($M^+$ − Et, 22.2), 198 ($M^+$ − OEt, 12.1), 170 ($M^+ - CO_2Et$ or $SiMe_3$, 89.7), 156 (13.4), 142 (24.1), 128 (11.2), 114 (15.8), 103 (21.2), 73 ($SiMe_3$ or $CO_2Et$, 100.0) and 59 (44.4) (Found: C, 59.2; H, 10.4; N, 5.3. $C_{12}H_{25}NO_2Si$ requires: C, 59.2; H, 10.4; N, 5.7%).

**1-Methoxycarbonyl-2-trimethylsilylaziridine, 12.**[9] Vinyltrimethylsilane (1.0 g, 10.0 mmol) and methyl azidoformate (1.01 g, 10 mmol) were irradiated continuously for 24 hours in a quartz tube. The resultant mixture was evaporated and purified by chromatography on silica with pentane as the eluent. The product, l-methoxycarbonyl-2-trimethylsilylaziridine was obtained as a colourless oil (0.55 g, 2.49 mmol, 24.9%); $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) −0.062 (9H, s, $Me_3Si$), 1.55 (1H, dd, *J* 7.33, 5.12, CHSi), 1.93 (1H, dd, *J* 1.22, 3.9, C$H_aH_b$), 2.27 (1H, dd, *J* 1.22, 7.33, $CH_aH_b$) and 3.73 (3H, 5, $OCH_3$); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) −3.3 ($Me_3Si$), 28.3 (CSi), 28.6 ($CH_2$), 53.4 ($OCH_3$) and 164.8 (C=O).

**1-Ethoxycarbonyl-2-(dimethylvinylsilyl)aziridine, 13.** Divinyldimethylsilane (2.0 g, 17.9 mmol) and ethyl azidoformate (2.1 g, 18.3 mmol) were irradiated continuously for 4 days in a quartz tube. The resultant mixture was evaporated and purified by chromatography on silica with pentane as the eluent. The product, 1-ethoxycarbonyl-2-(dimethylvinylsilyl)aziridine was obtained as a clear oil (1.9 g, 9.55 mmol, 53%). NMR spectroscopy shows that the product is a mixture of diastereoisomers which are present in roughly equal amounts; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) −0.021 and 0.010 (6H, 2 × s, $Me_2Si$), 1.11 (3H, t, $CH_2CH_3$), 1.55 (1H, dd, *J* 7.33, 5.13, $H_c$), 1.92 (1H, dd, *J* 1.22, 5.13, $H_a$), 2.23 (1H, dd, *J* 1.22, 7.08, $H_b$), 3.97 (2H, q, $CH_2$) and 5.74–6.04 (3H, m, $HC{=}CH_2$); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) −5.3 and −5.0 ($Me_2Si$), 14.3 ($CH_3$), 26.9 (CSi), 28.2 ($NCH_2$), 62.0 ($CH_2CH_3$), 133.8 ($HC{=}CH_2$), 135.7 ($H_2C{=}CH$) and 163.8 (C=O); *m*/*z* (EI) 200 ([M + H]$^+$, 18.6%), 173 ([M + H]$^+$ − $H_2C{=}CH$, 15.2), 172 ($M^+ - H_2C{=}CH$, 35.9), 126 ($M^+ - CO_2Et$, 42.7), 112 (25.9), 103 (44.2), 100 ($M^+ - CH_2CHSiMe_3$, 70.0), 87 (19.7), 86 ($CH_2CHSiHMe_2^+$, 42.1), 85 ($CH_2CHSiMe_2^+$, 69.7), 75 (41.1), 73 ($CO_2Et^+$, 26.6), 71 (27.2) and 59 (100.0) (Found: $M^+ - CH_3$, 184.0708 (EI). $C_8H_{14}NO_2Si$ requires *M*, 184.0794; Found: $M^+ - CO_2Et$, 126.0352. $C_6H_{12}$-NSi requires *M*, 126.0375).

**Bis(1-ethoxycarbonylaziridin-2-yl)dimethylsilane, 14.** 1-Ethoxycarbonyl-2-(dimethylvinylsilyl)aziridine (1.2 g, 6.0 mmol) and ethyl azidoformate (0.69 g, 6.0 mmol) were irradiated in a quartz tube for 48 hours. The product oil was purified by chromatography on silica. The column was eluted with neat hexane until all of the residual alkene had been collected before increasing the polarity gradually (up to 20% diethyl ether). Bis(1-ethoxycarbonylaziridin-2-yl)dimethylsilane was obtained in the later fractions as a colourless oil (0.5 g, 0.174 mmol, 28.9%). The product was present as a mixture of diastereoisomers as indicated by the $^{13}C$ NMR spectrum; $\delta_C$(400 MHz, $CDCl_3$, $Me_4Si$) 0.00 ($Me_2Si$), 14.03 (2 × $CH_2CH_3$), 25.74 and 26.02 ($CHSiMe_2$), 28.49 ($CH_2N$), 62.50 ($CH_2O$) and 164.12 (C=O); *m*/*z* (EI) 287 ([M + H]$^+$, 17.9%), 271 ($M^+$ − Me, 4.7), 246 (15.4), 172 ([M − $EtO_2CNCH_2CH_2]^+$, 100.0), 103 (22.6), 100 (60.1), 85 (17.1), 75 (23.7) 59 (28.4) and 29 (81, Et) (Found: $M^+ - CH_3$, 271.1114 (EI). $C_{11}H_{19}NO_4Si$ requires *M*, 271.1111).

**1-Phenyl-2-trimethylsilylaziridine, 15, with solvent.** Phenyl azide (3.2 g, 26.9 mmol) and vinyltrimethylsilane (5.4 g, 53.8 mmol) in 10 ml hexane were placed in a 20 ml quartz tube and mounted in a Rayonet photochemical reactor. The solution was irradiated using a medium pressure arc (*ca.* 5.5 W) for 5 h. The product was analysed by NMR spectroscopy which indicated the presence of product and intermediate triazoline $\delta_H$($CDCl_3$) 0.14 ($SiMe_3$), 3.10–4.20 (complex pattern, non-aromatic H's), 6.40–7.50 (phenyl H's) in a 1 : 1 ratio. Further irradiation or recharging with vinylsilane failed to improve the ratio. Overall yields were low due to evaporation of the vinylsilane within the cell which was known to reach 40 °C. Heating the aziridine–triazoline mixtures had no effect.

**1-Phenyl-2-trimethylsilylaziridine, 15, without solvent.** A mixture of phenyl azide (0.50 g, 4.20 mmol) and vinyltrimethylsilane (0.80 g, 8.00 mmol) was placed in a quartz UV cuvette and mounted in a Rayonet photochemical reactor. The solution was irradiated using a medium pressure arc (*ca.* 5.5 W) for 1 h. A brown–orange solution was obtained and analysed by $^1H$ NMR. The mixture afforded 1-phenyl-2-trimethylsilyl-1,2,3-triazoline (70%) and 1-phenyl-2-trimethylsilylaziridine (30%). After 3 h irradiation, the reaction mixture afforded 1-phenyl-2-trimethylsilylaziridine (50%).

### General procedure for the synthesis of aziridines by the thermolysis of phenyl azide in the presence of vinylsilanes

Aziridines were synthesized by the thermolysis of phenyl azide in the presence of vinyltrimethylsilane, methyl 2-(triethylsilyl)-propenoate and methyl 2-(dimethylphenylsilyl)propenoate under an identical set of conditions. A general method is described for the synthesis of 2-methoxycarbonyl-1-phenyl-2-(triethylsilyl)aziridine.

**Methyl 2-(dimethylphenylsilyl)propenoate.** A catalytic amount (0.2 g) of 10% platinum on carbon (or hexachloroplatinic acid) was added to a stirring solution of dimethylphenylsilane (3.10 g, 22.8 mmol) and methyl propynoate (1.92 g, 22.8 mmol). A mildly exothermic reaction was accompanied with weak effervescence. After 0.5 hours a substantial exotherm ensued accompanied by the development of a dark brown colour. The catalyst was removed by precipitation in hexane. The crude product comprised methyl 2-(dimethylphenylsilyl)-propenoate (70%) the remainder being the vicinal adduct, methyl (*E*)-3-(dimethylphenylsilyl)propenoate. Pure methyl 2-(dimethylphenylsilyl)propenoate (3.2 g, 14.6 mmol, 64.2%) was obtained by chromatography on silica, with hexane as the eluent. The product appeared in the later fractions; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 0.41 ($Me_2Si$), 3.61 (3H, s, $OCH_3$), 5.92 (1H, d, *J* 2.93, $H_aH_bC{=}$), 6.80 (1H, d, *J* 2.93, $H_aH_bC{=}$), 6.796–6.803 and 7.29–7.50 (5H, m, Ph); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) −2.2 (MeSi), 1.5 (MeSi), 52.2 (OMe), 128.4, 129.9 and 141.9 (Ph), 134.2 and 134.6 ($H_2C{=}$ and $SiC{=}$), 170.0 (C=O) (Found: C, 66.3; H, 7.5. $C_{12}H_{16}O_2Si$ requires C, 66.4; H, 7.3%).

**Methyl 2-(diphenylmethylsilyl)propenoate.** This was prepared by the same method as for methyl 2-(dimethylphenylsilyl)-propenoate. The product mixture consisted of 60% of the geminal isomer (methyl 2-(diphenylmethylsilyl)propenoate) and 40% of the vicinal isomer (methyl (*E*)-3-(diphenylmethylsilyl)-propenoate). A hexane solution yielded a yellow solid such that almost pure methyl 2-(diphenylmethylsilyl)propenoate was recovered from the mother liquor. Successive cooling of the

mother liquor in stages yielded a yellow oil which was further purified by flash column chromatography; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 0.46 (3H, 5, MeSi), 3.19 (3H, s, $OCH_3$), 5.53 (1H, d, *J* 1.20, $H_aH_bC$=), 6.48 (1H, d, *J* 1.20, $H_aH_bC$=) and 6.70–7.20 (10H, m, $Ph_2Si$) (Found C, 72.0; H, 6.5. $C_{17}H_{18}O_2Si$ requires C, 72.3; H, 6.4%).

**2-Methoxycarbonyl-1-phenyl-2-triethylsilylaziridine, 16.** A 60:40 mixture of methyl 2-(triethylsilyl)propenoate (15 g, 45 mmol) and methyl (*E*)-3-(triethylsilyl)propenoate[8] was heated to 110–120 °C in the presence of phenyl azide (5.35 g, 45 mmol). Heating was continued until evolution of nitrogen had subsided (*ca.* 2 hours). All of the methyl 2-(triethylsilyl)propenoate reacted to give 2-methoxycarbonyl-1-phenyl-2-triethylsilylaziridine and the vicinal alkene remained mostly unreacted. The residual alkene was removed by chromatography on silica, and the product aziridine purified by distillation (bp, 110–117 °C, 0.1 mmHg) to give pure 2-methoxycarbonyl-1-phenyl-2-triethylsilylaziridine (9.8 g, 31.5 mmol, 70%); $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 0.68–0.84 (6H, m), 0.90–1.54 (9H, m), $Et_3Si$, 2.40 (1H, d, *J* 1.60, $NCH_aH_b$), 2.76 (1H, d, *J* 1.60, $NCH_aH_b$), 3.44 (3H, s, OMe) and 6.83–7.16 (5H, m, Ph); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) 2.3 ($3 \times CH_2Si$), 7.9 ($3 \times CH_3CH_2Si$), 35.6 (NCSi), 36.9 ($CH_2N$), 51.5 ($CH_3O$), 120.6, 123.1, 128.5 and 150.7 (Ph) and 172.0 (C=O) (Found: $M^+$, 291.1699 (EI). $C_{16}H_{25}NO_2Si$ requires *M*, 291.1655) (Found: C, 65.7; H, *8.8; N, 4.5.* $C_{16}H_{25}NO_2Si$ requires C, 65.9; H, 8.7; N, 4.8%).

**2-Methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine, 17.** This was prepared using methyl 2-(dimethylphenylsilyl)-propenoate (2.0 g, 80%, 7.27 mmol) and phenyl azide (0.87 g, 7.31 mmol) to give, after purification by column chromatography, pure 2-methoxycarbonyl-2-dimethylphenylsilyl-1-phenylaziridine as a colourless viscous oil (2.0 g, 6.43 mmol, 88%); $\nu_{max}$(neat)/$cm^{-1}$ 3100, 2810, 1740, 1710, 1595, 1490, 1430, 1240, 1110, 835, 815 and 700; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 0.30 and 0.38 ($2 \times 3H$, $2 \times$ s, $Me_2Si$), 2.22 (1H, s, $NCH_aH_b$), 2.67 (1H, s, $NCH_aH_b$), 3.21 (3H, s, $OCH_3$) and 6.66–7.49 (10H, m, NPh and SiPh); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) −4.0 and −3.7 ($Me_2Si$), 35.9 (CSi), 38.1 ($CH_2$), 51.8 ($CH_3$), 120.8, 123.0, 128.4, 129.2, 129.7, 134.8, 136.6 and 150.8 (CPh and NPh), 170.6 (C=O) (Found: C, 69.4; H, 6.9; N; 4.0. $C_{18}H_{21}NO_2Si$ requires C, 69.4; H, 6.8; N, 4.5%).

**1-Phenyl-2-trimethylsilylaziridine, 15, with solvent.** The mixture of phenyl azide (1.0 g, 8.39 mmol) and vinyltrimethylsilane (3.30 g, 33.0 mmol) in hexane (5 ml) was heated under reflux at 60 °C under nitrogen (3 h). The orange–yellow reaction mixture was concentrated to dryness. TLC, using hexane as an eluent, showed the presence of phenyl azide, aziridine and a new product. GLC showed the presence of three major components. A sample (0.73 g) was purified on a silica column using hexane–diethyl ether (11:1) as eluent. Separation afforded 1-phenyl-2-trimethylsilylaziridine (0.15 g, 19%); $\nu_{max}$/(neat) $cm^{-1}$ 3100–2896, 1595, 1490, 1335, 1155, 925, 840, 750 and 690; $\delta_H$(400 MHz, $CDCl_3$, $Me_4Si$) 0.10 (9H, s, $SiMe_3$), 1.30 (1H, dd, CH), 2.10 (2H, m, *J* 7.5, 5.0, 1.7, $CH_2$) and 6.70–7.40 (5H, m, Ph); $\delta_C$(100 MHz, $CDCl_3$, $Me_4Si$) −3.16 ($SiMe_3$), 29.36 ($CHSiMe_3$), 31.14 ($=CH_2$), 121.04, 122.02, 128.68 and 156.43 (Ph) (Found: C, 69.0; H, 8.9; N, 7.3. $C_{11}H_{17}NSi$ requires C, 69.0; H, 9.0; N, 7.3%).

**1-Phenyl-2-trimethylsilylaziridine, 15, without solvent.** Phenyl azide (2.93 g, 17.1 mmol) and vinyltrimethylsilane (3.42 g, 34.2 mmol) were placed in a round bottomed flask and stirred under reflux at 55 °C for 8 h, and then stirred for a further 48 h at room temperature. The dark yellow solution was washed in brine, extracted with ether, dried and evaporated. The product was distilled under reduced pressure (bp 70–75 °C/0.1 mmHg) to give as a deep yellow oil 1-phenyl-2-trimethylsilylaziridine (2.00 g, 61.2%).

***trans*-3-Butyl-2-trimethylsilylaziridine, 5, by the reduction of *trans*-3-butyl-1-ethoxycarbonyl-2-trimethylsilylaziridine.** A solution of *trans*-3-butyl-1-ethoxycarbonyl-2-trimethylsilylaziridine (0.28 g, 1.07 mmol) in dry ether (3 ml) was added dropwise over a 10 minute period to a stirring slurry of lithium aluminium hydride (0.13 g, 3.42 mmol) in ether (20 ml) at 0 °C. The mixture was stirred for a further 1 h at 0 °C and allowed to warm to room temperature and stirred overnight. The grey coloured reaction mixture was again cooled to 0 °C and hydrolysed by dropwise addition of water (3 ml). The mixture was stirred rapidly for 30 minutes. The resultant white solid was washed with small portions of ether and the ethereal solution dried. The solvent was distilled from the product to give a pungent, pale yellow oil. This was further purified by flash column chromatography on silica, using pentane as the eluant, to give *trans*-3-butyl-2-trimethylsilylaziridine as a clear oil (0.139 g, 0.628 mmol, 59%).

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