Aziridination of Phenylalkenylsilanes and Phenylalkenylstannanes

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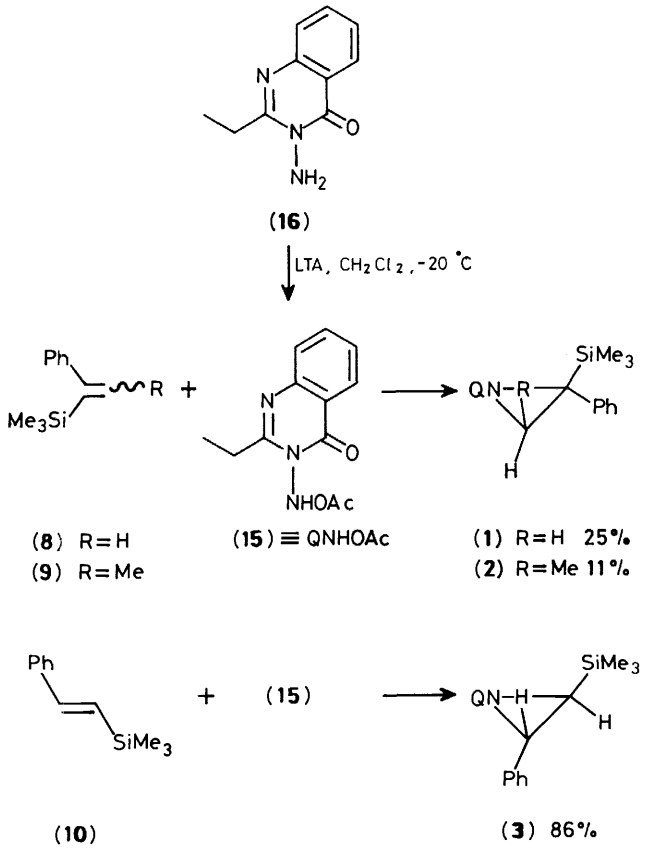
The phenylalkenylsilanes (**8**)—(**10**), phenylalkenylstannanes (**11**)—(**13**), and 2-triphenylstannylpropene (**14**) have been aziridinated using *N*-acetoxyaminoquinazolone (**15**). Relative configurational assignments at positions 1 (invertomers), 2, and 3 on the aziridine ring have been made which suggest that an attractive interaction is present between the quinazolone ring carbonyl oxygen and the tin atom in the aziridines (**4**)—(**7**).

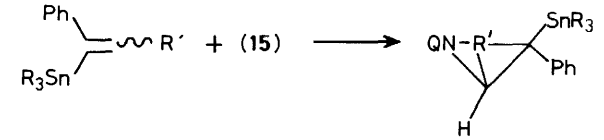
Although 1-silyl- or 1-stannyl-aziridines are well known, the corresponding 2- or 3- isomers are not. The limited number of 2-silylaziridines which have been reported have been obtained by 1,3-dipolar addition of azides to alkenylsilanes followed by elimination of nitrogen or by addition of halogen azides or pseudohalogens (Cl_2NHCO_2Et) to alkenylsilanes followed by reduction and ring-closure.[1]

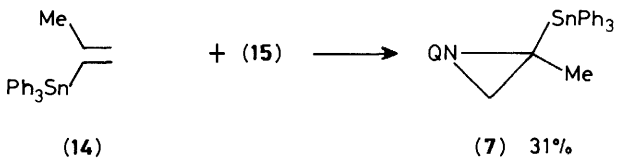
The chemistry of these 2- or 3-silyl-substituted aziridines has not been investigated: a literature search revealed no examples of 2- or 3-substituted stannylaziridines.



We have prepared the silylaziridines (**1**)—(**3**) and the stannylaziridines (**4**)—(**6**) by aziridination of the corresponding phenylalkenylsilanes (**8**)—(**10**) and phenylalkenylstannanes (**11**)—(**13**). Similarly, 2-methyl-2-triphenylstannylazirdine (**7**) was obtained by aziridination of 2-triphenylstannylpropene (**14**).

The alkenyl-silanes and -stannanes required were obtained using the Shapiro reaction from the corresponding ketone benzenesulphonylhydrazones followed by silylation or stannylation; (**14**) was similarly prepared using acetone 2,4,6-triisopropylbenzenesulphonylhydrazone. β-Trimethylsilylstyrene (**10**) was prepared from benzaldehyde, bis(trimethylsilyl)-methane, and butyl-lithium using a Peterson elimination.[2] The alkenylsilane (**9**) and the alkenylstannanes (**12**) and (**13**) were obtained as mixtures of double bond isomers and were used in the aziridinations as such.





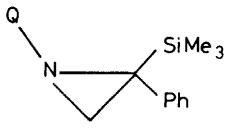
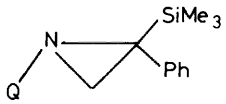
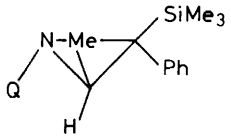
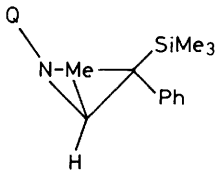
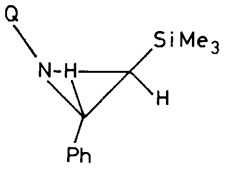
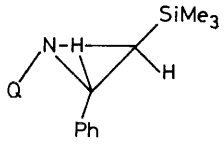
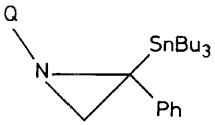
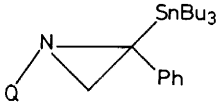
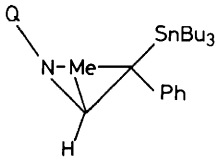
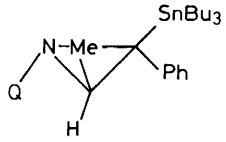
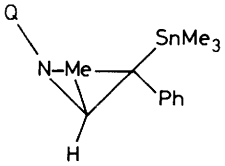
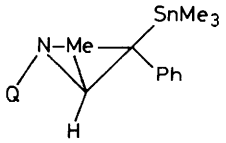
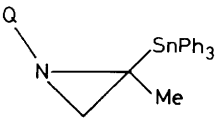
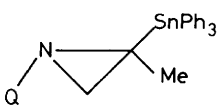
The vinylcarbanion in the Shapiro reaction reacts with tributylstannyl chloride and trimethylstannyl chloride to give similar ratios of double bond isomers of (**12**) and (**13**) (~3:1). The $^{119}SnC{=}CH$ coupling constants of major and minor isomers in *e.g.* (**12**) are 125 and 66 Hz, respectively and hence the major isomers have the *Z*-configuration since the size of this coupling constant is invariably greater for the *trans* $SnC{=}CH$ arrangement than for the *cis*.[3]

Aziridinating agent (**15**) was prepared, *in situ*, from the *N*-aminoquinazolone (**16**) by oxidation with lead tetra-acetate (LTA)[4] and the alkenyl-silane or -stannane was added subsequently. This procedure is particularly useful for aziridination of alkenes which would otherwise be attacked by LTA. We found subsequently, however, that these alkenylsilanes are sufficiently stable to LTA to allow aziridination to be carried out by oxidation of *N*-aminoquinazolone (**16**) in their presence.

The aziridines (**1**)—(**7**) are reasonably stable and, with the exception of (**4**), are crystalline solids elucidation of whose relative configuration at C-2 and C-3 [for cases of (**2**), (**5**), and (**6**)] presented problems. In addition, all of them with the exception of (**4**) and (**7**) showed the presence of both invertomers at the aziridine ring nitrogen in their n.m.r. spectra.

Assignment of configuration at C-2 and C-3 in aziridine (**6**) is secure since the yield of this product (64%) is such that it must

Table. Invertomer ratios and selected chemical shifts for aziridine ring methyl groups and quinazolone 5-H from the n.m.r. spectra of the aziridines (1)—(7)

Aziridine	Major invertomer	Minor invertomer	Invertomer ratio major : minor
(1)			13 : 1
	δ 5–H 8.26	7.99	
(2)			5 : 1
	δ 5–H 7.88 δ azir. Me 1.72	8.22 1.45	
(3)			1.8 : 1
	δ 5–H 8.28	8.34	
(4)			> 50 : 1
	δ 5–H 8.22		
(5)			4 : 1
	δ 5–H 8.21 δ azir. Me 1.36	7.98 1.68	
(6)			8 : 1
	δ 5–H 8.18 δ azir. Me 1.38	7.9 1.65	
(7)			> 50 : 1
	δ 5–H 7.79		

be derived from the more abundant *Z*-isomer of the alkenylstannane (**13**). The assumption is made here that aziridination proceeds with retention of configuration of the alkenylsilane but this is always without exception found to be the case for addition to other alkenes. The other (*E*)-isomer of the alkenylstannane (**13**) is apparently unreactive towards (**15**) (see below).

Supporting evidence for the configuration of (**6**) as shown is the n.O.e. between the *ortho*-protons of the phenyl ring and the aziridine ring proton at the 2-position (and the absence of any n.O.e. between the same phenyl ring protons and the azirdine ring methyl group).

The aziridine (**5**) exists as a 4:1 ratio of invertomers at nitrogen whose interconversion is slow on the n.m.r. time-scale. Assignment of invertomers to the two species whose signals are present in the n.m.r. spectrum [and not rotamers around the N–N bond (see below) or even configurational isomers at C-2,3] comes from the disappearance of signals from the minor invertomer when the crystalline material is dissolved in $CDCl_3$ at −55 °C and the n.m.r. spectrum run at this temperature: the equilibrium ratio of 4:1 is re-established when the temperature of the sample is raised to ambient before the spectrum is re-run at −55 °C. Similarly, a crystalline sample of (**6**), dissolved at −40 °C shows a 16:1 ratio of invertomers at this temperature which changes to an equilbrium value of 8:1 after the sample is warmed to ambient temperature before re-running of the spectrum at −40 °C. This behaviour is typical of other aziridines we have encountered which crystallise as one pure (or almost pure) invertomer and are configurationally stable in nitrogen at −40 °C but invert increasingly rapidly above ~0 °C.[5]

The major invertomer in (**6**) was assigned the configuration having the quinazolone and phenyl rings *trans*: this is in agreement with empirical shielding and deshielding effects which the quinazolone ring has on the *cis*-aziridine ring methyl and *cis*-aziridine ring proton(s) respectively.[6] A further shielding effect on the quinazolone 5-H by a phenyl ring *cis*-substituted on the aziridine ring was observed in the minor invertomers in (**1**), (**5**), and (**6**) and the major invertomer in (**2**): it appears that this effect requires the butressing of a *gem*-trisubstituted silyl or stannyl substituent to operate since it is absent in (**3**). The chemical shift of 5-H in the quinazolone ring is also shifted upfield from its expected position in the single invertomer of (**7**) which is attributable to the shielding effect of one of the phenyl rings in the triphenyltin substituent.

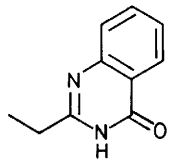
A summary of invertomer ratios and selected chemical shifts of (**1**)–(**7**) is given in the Table. It will be noted that the change in invertomer ratio from 4:1 to 8:1 in (**5**) and (**6**), respectively, is consistent with the smaller effective bulk of the stannyl substituent in (**6**).

It is clear from the ratios given in the Table that invertomers having the stannyl substituent *cis* to the quinazolone ring are stabilised relative to their silyl analogues: it seems likely that this is the result of a relatively stronger attractive interaction between the (quinazolone ring) carbonyl oxygen and the tin atom.[7]

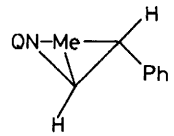
Signals from the aziridine ring protons in the minor invertomers of (**5**) and (**6**) show considerable broadening at room temperature which we attribute to rotation around the N–N bond becoming slow on the n.m.r. time-scale.[8] Significantly, the corresponding signals from the major invertomers in these aziridines are sharp even at −40 °C which we believe is due to the presence of single rotamers around the N–N bond as a result of 'anchoring' by the carbonyl–tin interaction referred to above.

The yields of these aziridines (**1**)—(**7**) indicate that the reaction is sensitive to the degree of coplanarity which the phenyl group has with the double bond.* Thus for the case of (**10**), there is little impediment to the attainment of this conformation and the yield of the aziridine (**3**) is excellent (85%). The increase in yield with diminishing size of the alkyl substituent on tin [(**5**) ⟶ (**6**)] can be similarly explained. It is presumably the same lack of coplanarity between the phenyl ring and the double bond which accounts for the absence of any aziridination products from the *E*-isomers in (**9**), (**12**), and (**13**): this absence of coplanarity militates against the operation of an attractive interaction between the phenyl group and the quinazolone ring which is believed to be important in these aziridinations.[10]

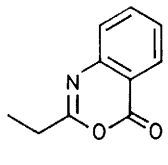
The major product in those aziridinations which proceeded in poor yields was the de-aminated quinazolone (**17**), the bulk of which was separated by trituration of the crude reaction



(**17**)



(**18**)



(**19**)

mixture with cold ether. However, in the aziridination of the alkenylsilane (**9**), the major product was the aziridine (**18**) (55%) which probably arises by acetic acid-mediated de-silylation of (**9**). A minor product (9%) isolated by chromatography in the aziridination of the alkenylstannane (**12**) was identified as the benzoxazinone (**19**), an authentic sample of which was obtained by heating a mixture of anthranilic acid and propionic anhydride. One of the products from oxidation of *N*-aminophthalimide (in the absence of alkenes) is phthalic anhydride and benzoxazinone (**19**) may be formed from *N*-aminoquinazolone (**16**) by a similar mechanism.[11]

Experimental

Butyl-lithium was used as 2.5M solution in hexane (Aldrich). N.m.r. spectra of compounds containing trialkylsilyl groups were run in $CDCl_3$ with CH_2Cl_2 or $CHCl_3$ as an internal standard at 300 MHz unless otherwise indicated. Other n.m.r. spectra were also run in $CDCl_3$ at 300 MHz unless otherwise indicated. Light petroleum refers to the fraction boiling at 60—80 °C throughout. Phenylalkenyltrimethylsilanes (**8**) and (**9**) were prepared from the corresponding benzenesulphonylhydrazones[12] using the Shapiro reaction[13] followed by addition of trimethylsilyl chloride: trimethyl-1-phenylvinylsilane (**8**) was obtained in 70% yield, b.p. 73—78 °C/5 mmHg (lit.,[14] b.p. 70—72 °C/10 mmHg); trimethyl-1-phenylpropenylsilane (**9**) was obtained in 67% yield, b.p. 68—72 °C/1 mmHg (lit.,[14] b.p. 73—75 °C/4 mmHg) as a 3:1 ratio of double bond isomers; δ_H(90 MHz) 7.6—6.9 (m, ArH), 6.2 [q, *J* 7 Hz, =CH (major)], 6.1 [q, *J* 7 Hz, =CH (minor)], 1.9 [d, *J* 7 Hz, Me (major)], 1.55 [d, *J* 7 Hz, Me (minor)], 1.5 [s, $SiMe_3$ (major)], and 0.5 [s, $SiMe_3$ (minor)]; trimethyl-2-phenylvinylsilane (**10**) was obtained by the method of Fleming *et al*.[2] in 69% yield b.p. 32—34 °C/0.05 mmHg (lit.,[15] 83—85 °C/6 mmHg). Phenylalkenyltributylstannanes (**11**)—(**13**) were obtained from the corresponding benzenesulphonylhydrazones[12] using the Shapiro reaction[13] followed by addition of tributylstannyl chloride or trimethylstannyl chloride: tributyl-1-phenylvinylstannane (**11**) was obtained in 57% yield b.p. 120—125 °C/1 mmHg (lit.,[16] b.p. 135 °C/1 mmHg); tributyl-1-phenylpropenylstannane (**12**)[17] was obtained as a 3:1 ratio of double bond isomers in 60% yield after purification by chromatography over silica gel with light petroleum as eluant δ_H(90 MHz) 7.5—

* This effect has been previously observed in other substituted styrenes: see ref. 9.

6.8 (m, ArH), 6.25 [q, *J* 6.2 Hz, =CH (major)], 5.8 [q, *J* 6.2 Hz, =CH (minor)], and 1.9—0.6 [m, $(CH_2)_3Me$]; trimethyl-1-phenylpropenylstannane (**13**) was obtained in 53% yield as a 3:1 ratio of double bond isomers, b.p. 75—80 °C/1 mmHg: the compound deteriorated with time and was used for aziridination within 24 h; δ_H(90 MHz) 7.6—6.9 (m, ArH), 6.54 ([q, *J* 7 Hz, =CH, (major)], 5.95 [q, *J* 7 Hz, =CH, (minor)], 1.95 [d, *J* 7 Hz, Me, (major)], 1.7 [d, *J* 7 Hz, Me minor)], 0.45 [s, $SnMe_3$, (major)], and 0.3 [s, $SnMe_3$, (minor)]. Triphenyl-2-propenylstannane (**14**) was prepared from the corresponding tri-isopropylbenzenesulphonylhydrazone[18] using the Shapiro reaction[13] followed by addition of triphenylstannyl chloride and obtained in 76% yield as a colourless solid m.p. 69—72 °C (lit.,[19] m.p. 77—79 °C.).

Aziridination of Alkenyl-silanes and -stannanes.—Powdered 3-amino-2-ethylquinazolin-4(3*H*)-one (**12**) (1 mol equiv.) and acetic acid-free lead tetra-acetate (1.05—1.1 mol equiv.) were added alternatively and continuously in very small portions over 15 min to a vigorously stirred solution of dry dichloromethane (1 ml/100 mg of *N*-aminoquinazolone) at −25 °C. After the mixture had been stirred for a further 30 min at this temperature, the alkenyl-silane or -stannane (1.5—3.5 mol equiv.) was added and the solution allowed to warm to ambient temperature. The solution was filtered to remove lead di-acetate, the lead di-acetate washed with dichloromethane, and the filtrate washed successively with sodium hydrogen carbonate solution and water, dried, and evaporated under reduced pressure.

Compound (**8**). Aziridination of (**8**) (0.349 g, 1.98 mmol) using the above procedure with (**12**) (0.25 g, 1.32 mmol) and LTA (0.616 g, 1.38 mmol) in dichloromethane (2.5 ml) gave, after chromatography of the crude reaction product over silica gel with ethyl acetate–light petroleum (1:2) as eluant *2-ethyl-3-(2-phenyl-2-trimethylsilylaziridin-1-yl)quinazolin-4(3H)-one* (**1**) as colourless crystals (0.12 g, 25%), m.p. 108—110 °C (from petroleum) (Found: C, 69.55; H, 7.05; N, 11.5. $C_{21}H_{25}N_3OSi$ requires C, 69.4; H, 6.95; N, 11.55%); δ_H(major invertomer: Q and $SiMe_3$ *cis*), 8.26 (ddd, *J* 7.9, 1.4, and 0.6 Hz, Q 5-H), 7.72 (ddd, *J* 8, 7.4, and 1.4 Hz, Q 7-H), 7.65 (ddd, *J* 8, 1.3, and 0.6 Hz, Q 8-H), 7.45 (ddd, *J* 8, 7.4, and 1.3 Hz, Q 6-H), 7.72—7.27 (m, 5 × ArH), 3.17 (dq, *J* 16 and 7.5 Hz, *H*CHMe), 3.06 (d, *J* 1.2 Hz, azir. 3-H *cis* to Q), 3.04 (dq, *J* 16 and 7.5 Hz, HC*H*Me), 2.65 (d, *J* 1.2 Hz, azir. 3-H *trans* to Q), 1.42 (t, *J* 7.5 Hz, CH_2Me), and −0.1 (s, $SiMe_3$); (minor invertomer: Q and $SiMe_3$ *trans*), 7.8 (dd, *J* 7.9 and 1.4 Hz, Q 5-H), 7.57 (ddd, *J* 8, 7.4, and 1.4 Hz, Q 7-H), and 0.19 (s, $SiMe_3$) (other signals obscured by major invertomer). The ratio of major:minor invertomers was 13:1 at room temperature, $\nu_{max.}$ 1 660s and 1 585s cm^{-1}; *m/z* (%) 363 (M^+, 8), 348 (5), 334 (52), 246 (14), 245 (26), 231 (22), 200 (37), 176 (16), 175 (17), 174 (26), 173 (13), 157 (16), 147 (11), 135 (12), 131 (12), 130 (21), 117 (25), 103 (13), and 73 (100).

Compound (**9**). Aziridination of (**9**) (1.5 g, 7.93 mmol) using the above procedure with (**12**) (0.5 g, 2.64 mmol) and LTA (1.23 g, 2.77 mmol), in dichloromethane (5 ml) gave, after chromatography of the crude product over silica gel with ethyl acetate–light petroleum (1:3 as eluant, *(Z)-2-ethyl-3-(2-methyl-3-phenyl-3-trimethylsilylaziridin-1-yl)quinazolin-4(3H)-one* (**2**) as colourless crystals (75 mg, 11%), m.p. 111—114 °C (from light petroleum) (Found: M^+, 377.1915. $C_{22}H_{27}N_3OSi$ requires M^+, 377.1923) δ_H(major invertomer: Q and Ph *cis*) 7.88 (d, *J* 8 Hz, Q 5-H), 7.57 (ddd, *J* 8.1, 7.3, and 1.4 Hz, Q 7-H), 7.52 (dd, *J* 8.1 and 1.2 Hz, Q 8-H), 7.25 (ddd, *J* 8, 7.3, and 1.2 Hz, Q 6-H), 7.2—6.9 (m, 5 × ArH), 4.72 (br s, azir. 2-H *cis* to Q), 3.47 (br dq, *J* 16 and 7 Hz, *H*CHMe), 3.1 (dq, *J* 16 and 7 Hz, HC*H*Me), 1.72 (d, *J* 6.5 Hz, CH*Me*), 1.51 (t, *J* 7 Hz, CH_2Me), and 0.18 (s, $SiMe_3$) (minor invertomer: Q and Ph *trans*), 8.22 (d, *J* 8 Hz, Q 5-H), 1.45 (d, *J* 6.5 Hz, CH*Me*), 1.36 (t, *J* 7 Hz, CH_2Me), and 0.01 (s, $SiMe_3$) (other signals obscured). The ratio of major:minor invertomers at room temperature was 5:1; $\nu_{max.}$ 1 665s and 1 595s cm^{-1}; *m/z* (%) 377 (2), 348 (13), 274, (12), 245 (15), 231 (14), 214 (20), 204 (86), 176 (100), 162 (19), 157 (21), 147 (25), 137 (23), 130 (51), 119 (36), and 105 (74). Further elution with ethyl acetate–light petroleum (1:3) gave (E)-2-*ethyl*-3-(2-*methyl*-3-*phenylaziridin*-1-*yl*)*quinazolin*-4(3H)-*one* (**18**) (0.44 g, 55%) as colourless crystals, m.p 98—101 °C (from ethanol) identical with a sample prepared by aziridination of (*E*)-propenylbenzene using *N*-aminoquinazolone (**12**) and LTA as previously described[4] (Found: 74.55; H, 6.35; N, 13.7. $C_{19}H_{19}N_3O$ requires C, 74.7; H, 6.25; N, 13.75%); δ_H(major invertomer; Q and phenyl *trans*), 8.14 (ddd, *J* 8, 1.4, and 0.6 Hz, Q 5-H), 7.7—6.8 (m, 8 × ArH), 3.97 (d, *J* 6.0 Hz, azir. 3-H, *cis* to Q), 3.19 (dq, *J* 17 and 7 Hz; *H*CHMe), 2.91 (dq, *J* 17 and 7 Hz, HC*H*Me), 1.41 (t, *J* 7.0 Hz, CH_2Me), 1.3 (d, *J* 6.0 Hz, azir. Me *cis* to Q); the azir. 2-H signal was obscured by the signal at 2.91 p.p.m.; (minor invertomer: Q and phenyl *cis*), 8.15—6.8 (9 × ArH), 3.85 (m, azir. 2-H *cis* to Q), 3.49 (d, *J* 6.0 Hz, azir. 3-H, *trans* to Q), 2.35 (br dq, *J* 17 and 7 Hz, HC*H*Me), 1.7 (d, *J* 6.0 Hz, azir. Me), and 1.1 (t, *J* 7.0 Hz, CH_2Me); the *H*CHMe signal was obscured by the signal at 2.91 p.p.m. At room temperature the ratio of major:minor invertomers is 1.5:1; $\nu_{max.}$ 1 670s and 1 595s cm^{-1}; *m/z* (%) 305, (M^+, 5), 132 (100), 131 (42), and 105 (15).

Compound (**10**). Aziridination of (**10**) (1.39 g, 7.93 mmol) using the above procedure with (**12**) (0.5 g, 2.64 mmol) and LTA (1.23 g, 2.77 mmol) in dichloromethane (5 ml) gave, after chromatography of the crude product over silica gel using ethyl acetate–light petroleum (1:6) as eluant (E)-2-*ethyl*-3-(2-*phenyl*-3-*trimethylsilylaziridin*-1-*yl*)*quinazolin*-4(3H)-*one* (**3**) as a colourless oil (0.81 g, 86%) (Found: M^+, 363.1779. $C_{21}H_{25}N_3OSi$ requires M^+, 363.1767); δ_H(major invertomer; Q and $SiMe_3$ *cis*), 8.28 (ddd, *J* 8, 1.4, and 0.6 Hz, Q 5-H), 7.8—7.0 (m, Q 6-H, 7-H, and 8-H, 5 × ArH), 4.33 (d, *J* 7.5 Hz, azir. 2-H *cis* to Q), 3.27 (dq, *J* 18 and 7 Hz, *H*CHMe), 3.06 (dq, *J* 18 and 7 Hz, HC*H*Me), 2.27 (d, *J* 7.5 Hz, azir. 3-H *trans* to Q), 1.47 (t, *J* 7 Hz, CH_2Me), and 0.08 (s, $SiMe_3$); (minor invertomer; Q and $SiMe_3$ *trans*), 8.34 (d, *J* 8 Hz, Q 5-H), 3.58 [d, *J* 7.5 Hz, azir. 3-H (or 2-H)], 3.37 [d, *J* 7.5 Hz, azir. 2-H (or 3-H)], 2.49 (m, CH_2Me), 1.22 (t, *J* 7 Hz, CH_2Me), and 0.38 (s, $SiMe_3$). The ratio of major:minor invertomers at room temperature is 1.8:1; $\nu_{max.}$ 1 655s and 1 585s cm^{-1}; *m/z* (%) 363, (M^+, 11), 335 (56), 334 (100), 246 (22), 245 (45), 231 (22), 200 (50), 174 (55), 173 (43), 120 (22), 119 (25), 117 (29), and 105 (44).

Compound (**11**). Aziridination of (**11**) (2.49 g, 6.34 mmol) using the procedure above with (**12**) (0.6 g, 3.17 mmol) and LTA (1.47 g, 3.33 mmol) in dichloromethane (6 ml) gave, after chromatography of the crude oxidation product over silica gel with ethyl acetate–light petroleum (1:5) as eluant, *2-ethyl-3-(2-phenyl-2-tributylstannyl)quinazolin-4(3H)-one* (**4**) as a colourless oil (0.68 g, 37%) (Found: M^+, 582.2503. $C_{30}H_{44}N_3OSn$ requires M^+, 582.2506) δ_H(single invertomer: Q and $SnBu_3$ *cis*), 8.22 (ddd, *J* 7.9, 1.4, and 0.6 Hz, Q 5-H), 7.69 (ddd, *J* 8, 7.3, and 0.6 Hz, Q 7-H), 7.66—7.15 (m, Q 8-H and 5 × ArH), 7.43 (ddd, *J* 7.9, 7.3, and 1.3 Hz, Q 6-H), 3.16 (dq, *J* 17 and 7.5 Hz, *H*CHMe), 3.04 (dq, *J* 17 and 7.5 Hz, HC*H*Me), 3.02 (s, azir. 3-H, *cis* to Q), 2.63 (s, azir. 3-H, *trans* to Q), 1.40 (t, *J* 7.5 Hz, CH_2Me), and 1.5—0.5 (m, $SnCH_2Me$); $\nu_{max.}$ 1 665s and 1 595s cm^{-1}; *m/z* (%) 582 (M^+, ~1), 407 (100), 405 (80), 404 (45), 294 (45), 293 (42), 175 (20), 157 (45), and 118 (52).

Compound (**12**). Aziridination of (**12**) (2.58 g, 6.34 mol) using the procedure above with (**12**) (0.4 g, 2.11 mmol) in LTA (0.986 g, 2.22 mmol) in dichloromethane (4 ml) gave, after chromatography of the crude product over silica with ethyl acetate–light petroleum (1:4) as eluant, *(Z)-2-ethyl-(2-methyl-3-phenyl-3-tributylstannylaziridin-1-yl)quinazolin-4(3H)-one* (**5**) as colourless crystals (0.401 g, 32%), m.p. 53—56 °C (from ethanol) (Found: C, 62.7; H, 7.65; N, 7.1. $C_{31}H_{45}N_3OSn$ requires C, 62.65; H, 7.65;

N, 7.05%); δ_H (−40 °C) (major invertomer: Q and phenyl *trans*), 8.21 (ddd, *J* 1.3, and 0.6 Hz, Q 5-H), 7.77 (ddd, *J* 8, 7.3, and 1.3 Hz, Q 7-H), 7.67 (ddd, *J* 8, 1.4, and 0.6 Hz, Q 8-H), 7.65—7.10 (m, 5 × ArH), 7.4 (ddd, *J* 8, 7.3 and 1.4 Hz, Q 6-H), 3.21 (dq, *J* 16.5 and 7.5 Hz, *H*CHMe), 3.02 (q, *J* 6 Hz, azir. 2-H, *trans* to Q), 2.94 (dq, *J* 16.5 and 7.5 Hz, HC*H*Me), 1.38 (t, *J* 7.5 Hz, CH_2*Me*), 1.36 (d, *J* 6 Hz, CH*Me*), and 1.3—0.5 [m, Sn(CH_2)$_3$*Me*]; (minor invertomer; Q and phenyl *cis*), 7.98 (dd, *J* 8 and 1.4 Hz, Q 5-H), 4.47 (q, *J* 6 Hz, azir. 2-H *cis* to Q), and 1.68 (d, *J* 6 Hz, CH*Me*), other signals obscured. At room temperature, the ratio of major:minor invertomers is 4:1. A crystalline sample of this aziridine dissolved in $CDCl_3$ at −40 °C showed only signals from the major invertomer when the n.m.r. spectrum was run at −40 °C without any intermediate warming of the solution; $\nu_{max.}$ 1 665s and 1 597s cm^{-1}.

Further elution with ethyl acetate–light petroleum (1:4) gave 2-*ethyl*-3,1-*benzoxazin*-4-*one* (**19**) (35 mg, 9%) as a colourless crystalline solid, m.p. 77—79 °C (from light petroleum) (Found: C, 68.4; H, 5.3; N, 8.0. $C_{10}H_9NO_2$ requires C, 68.6; H, 5.2; N, 8.0%) δ_H 8.2 (ddd, *J* 8.0, 1.7, and 0.7 Hz, Q 5-H), 7.8 (ddd, *J* 8.8, 7.0, and 1.5 Hz, Q 7-H), 7.57 (ddd, *J* 8.8, 1.2, and 0.6 Hz, Q 8-H), 7.5 (ddd, *J* 8.0, 7.0, and 1.2 Hz, Q 6-H), 2.73 (q, *J* 7.5 Hz, CH_2Me), and 1.37 (t, *J* 7.5 Hz, CH_2*Me*); $\nu_{max.}$ 1 755s, 1 650s, and 1 600m cm^{-1}; *m/z* (%) 175, (M^+, 80), 146 (100), 120 (10), 119 (20), and 90 (30).

An authentic sample of (**19**) was prepared by heating anthranilic acid (1 equiv.) and propionic anhydride (2 equiv.) under reflux for 30 min. The solid obtained on cooling was crystallised from light petroleum to give (**19**) identical with that isolated above.

Compound (**13**). Aziridination of (**13**) (3.72 g, 7.92 mmol) using the procedure above with (**12**) (0.5 g, 2.64 mmol) and LTA (1.23 g, 2.77 mmol) in dichloromethane (5 ml) gave, after chromatography of the crude product over silica gel with ethyl acetate–light petroleum (1:3) as eluant (*Z*)-2-*ethyl*-(2-*methyl*-3-*phenyl*-3-*trimethylstannylaziridin*-1-*yl*)*quinazolin*-4(3H)-*one* (**6**) (0.79 g, 64%) as colourless crystals, m.p. 115—118 °C (from light petroleum) (Found: C, 56.55; H, 5.8; N, 8.95. $C_{22}H_{27}N_3OSn$ requires C, 56.45; H, 5.8; N, 8.95%); δ_H(−40 °C) (major invertomer: phenyl and Q *trans*), 8.18 (ddd, *J* 8, 1.4, and 0.5 Hz, Q 5-H), 7.75 (ddd, *J* 8, 7.3, and 1.4 Hz Q 7-H), 7.65 (ddd, *J* 8, 1.3, and 0.5 Hz, Q 8-H), 7.6—7.1 (m, 5 × PhH), 7.45 (ddd, *J* 8, 7.3, and 1.3 Hz, Q 6-H), 3.19 (dq, *J* 13.5 and 6 Hz, *H*CHMe), 3.02 (q, *J* 6 Hz, azir. 2-H *trans* to Q), 2.9 (dq, *J* 13.5 and 6 Hz, HC*H*Me), 1.38 (d, *J* 6 Hz, CH*Me*), 1.35 (t, *J* 6 Hz, CH_2*Me*), and −0.07 (s, $SnMe_3$); (minor invertomer; Q and phenyl *cis*), 7.9 (dd, *J* 7.8 and 1.4 Hz, Q 5-H), and 4.55 (br s, azir. 2-H *cis* to Q), 1.65 (d, *J* 6 Hz, CH*Me*), 1.82 (t, *J* 6 Hz, CH_2*Me*), and 0.53 (s, $SnMe_3$). At −40 °C the ratio of major:minor invertomers is 8:1. A crystalline sample of this aziridine dissolved in $CDCl_3$ at −40 °C showed the ratio of major:minor invertomers to be 16:1 when the n.m.r. spectrum was run at this temperature without any intermediate warming of the solution: $\nu_{max.}$ 1 665s and 1 595s cm^{-1}.

Compound (**14**). Aziridination of (**14**) (1.65 g, 4.23 mmol) using the procedure above with (**12**) (0.4 g, 2.11 mmol) and LTA (0.986 g, 2.22 mmol) in dichloromethane (4 ml) gave, after chromatography of the crude products over silica gel with ethyl acetate–light petroleum (1:4) as eluant, 2-*ethyl*-(2-*methyl*-2-*triphenylstannylaziridin*-1-*yl*)*quinazolin*-4(3H)-*one* (**7**) (0.38 g, 31%) as colourless crystals, m.p. 157—159 °C (from light petroleum) (Found: C, 64.35; H, 5.25; N, 7.25. $C_{31}H_{29}N_3OSn$ requires C, 64.5; H, 4.9; N, 7.25); δ 7.79 (ddd, *J* 8, 1.4, and 0.6 Hz, Q 5-H), 7.7—7.1 (m, Q 6-H, 7-H, and 8-H, 15 × Ar*H*), 3.04 (dq, *J* 7 and 1.5 Hz, CH_2Me), 2.95 (d, *J* 1.5 Hz, azir. 3-H *cis* to Q), 2.78 (d, *J* 1.5 Hz, azir. 3-H, *trans* to Q), 1.77 (s, Me), and 1.31 (t, *J* 7 Hz, CH_2*Me*); $\nu_{max.}$ 1 645s and 1 595s cm^{-1}.

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