Aziridination of alkenes with 3-acetoxyaminoquinazolinones in the presence of hexamethyldisilazane

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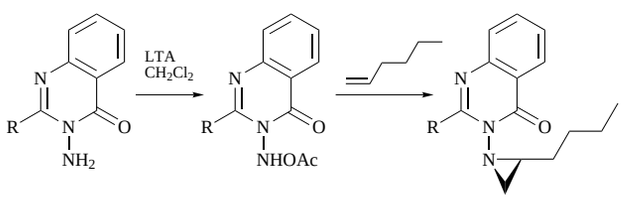
1 PERKIN

Yields of aziridines from reaction of some alkenes, including α,β-unsaturated esters, with 3-acetoxyamino-2-isopropylquinazolinone 6 (Q^3NHOAc) are greatly increased in the presence of hexamethyldisilazane (HMDS). A mono-aziridination product of naphthalene is obtained only in the presence of HMDS. It is concluded that the enhanced yields in these aziridinations are the result of scavenging of acetic acid by HMDS, thus prolonging the lifetime of the aziridinating agent Q^3NHOAc.

3-Acetoxyaminoquinazolinones *e.g.* **4** are aziridinating agents for alkenes.[1] High yields (>70%) of aziridines are obtained from certain alkenes *e.g.* styrene or methyl acrylate, even with only 1.5 equiv. of alkene. The 3-acetoxyamino-2-trifluoromethylquinazolinone **4** (Q^1NHOAc) is considerably more stable than its 2-alkyl substituted analogues *e.g.* **5** (Q^2NHOAc).[2] This stability is believed to account for the higher yields in aziridinations of less reactive alkenes using Q^1NHOAc **4**. Thus whereas the yield† of aziridine **8** from reaction of Q^2NHOAc **5** with hex-1-ene is <15%, aziridine **7** is obtained from Q^1NHOAc **4** in 50% yield under similar conditions (Scheme 1).[2]



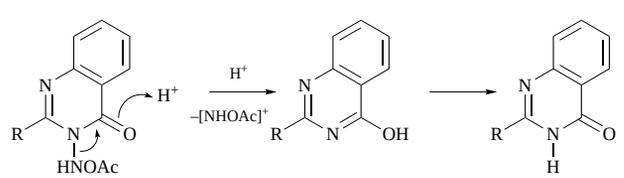
1 R = CF_3
2 R = Et
3 R = Pr^i

4 R = CF_3 = Q^1NHOAc
5 R = Et = Q^2NHOAc
6 R = Pr^i = Q^3NHOAc

7 R = CF_3 (50%)
8 R = Et (<15%)

Scheme 1

In the absence of alkene, decomposition of Q^2NHOAc **5** gives the 3*H*-quinazolinone **9** as the major product and this is also the major product in aziridination of less reactive alkenes *e.g.* hex-1-ene (as in Scheme 1). The rate of decomposition of Q^2NHOAc **5** is retarded by the removal of acetic acid—a by-product both in acetoxylation of the 3-aminoquinazolinone **2** with lead tetraacetate (LTA) and in the aziridination of alkenes by Q^2NHOAc **5**. Acetic acid is assumed to protonate the quinazolinone ring and facilitate cleavage of the N–N bond (Scheme 2); the fate of the acetoxyamino residue is not known.



9 R = Et
10 R = Pr^i

Scheme 2

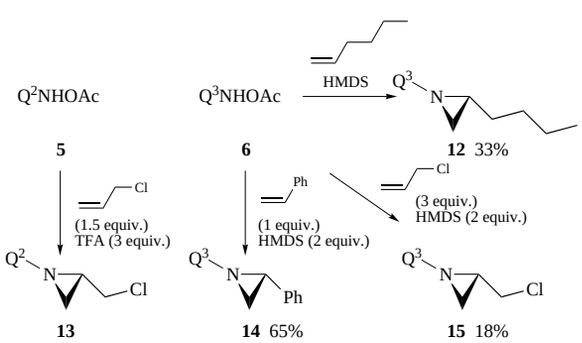
Our explanation for the increased stability of Q^1NHOAc **4** and the superior yields in its aziridination of alkenes is the diminished basicity of the quinazolinone ring resulting from the effect of the electron withdrawing trifluoromethyl group: the rate of decomposition of Q^1NHOAc **4** by a pathway analogous to that in Scheme 2 would therefore be slower. If this interpretation is correct then improved yields of aziridines should be obtained from 2-alkyl-substituted 3-acetoxyaminoquinazolinones *e.g.* Q^2NHOAc **5** if the acetic acid co-produced in the aziridination is removed as it is formed. Removal of the mol equivalent of acetic acid, produced in the acetoxylation of 3-aminoquinazolinone **2**, involves simply shaking a cold (*ca.* −10 °C) dichloromethane solution of Q^2NHOAc **5** (separated from lead diacetate at <−10 °C) with an ice-cold aqueous solution of sodium hydrogen carbonate.

Scavenging of acetic acid co-produced in the aziridination itself ideally requires a dichloromethane soluble base which does not react with Q^2NHOAc **5** under the reaction conditions. This rules out simple amines which react readily with *e.g.* Q^2NHOAc **5** by nucleophilic displacement of the acetoxy group from nitrogen;[3] using pyridine, for example the first formed pyridinium amide **11** is isolable (Scheme 3).[4]

5 **11**

Scheme 3

However, the presence of the trimethylsilyl groups in hexamethyldisilazane (HMDS) greatly reduced the nucleophilic character of the amine without inhibiting its reaction with (acetic) acid. We find that in the presence of HMDS, the yields of aziridines from reaction of 3-acetoxyamino-2-alkylquinazolinones and alkenes are improved, especially for otherwise less reactive alkenes. Thus, the yield of aziridine **14** from reaction of 3-acetoxyamino-2-isopropylquinazolinone **6** (Q^3NHOAc)[5] (1 equiv.) with styrene (1 equiv.) was raised from 56 to 65% in the presence of HMDS (2 equiv.) (Scheme 4) from NMR examin-



5 **6** **12** 33%

13 **14** 65% **15** 18%

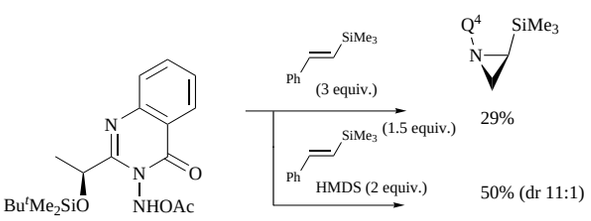
Scheme 4

† Unless otherwise indicated yields refer to those isolated.

ation of the crude reaction product. Reaction of Q^3NHOAc **6** with hex-1-ene (3 equiv.) gave aziridine **12** in 15% yield from NMR spectroscopy (Scheme 4). The same aziridination carried out in the presence of (HMDS) (2 equiv.) gave a 33% isolated yield of aziridine **12**. In this aziridination Q^3NHOAc **6** was prepared from the corresponding 3-aminoquinazolinone **3** at −20 °C and freed from lead diacetate but no attempt was made to remove the acetic acid co-produced in this acetoxylation. An increase in the number of mol equivalents of HMDS used in this aziridination of hex-1-ene from two to ten had no effect on the yield of aziridine **12**. The major product this attempted aziridination was, as expected, the corresponding 3*H*-quinazolinone **10**.

Examination of the crude product from attempted reaction of allyl chloride (3 equiv.) with Q^3NHOAc **6** showed <5% aziridine was present. In the presence of HMDS however, an 18% yield of aziridine **15** was isolated (Scheme 4).

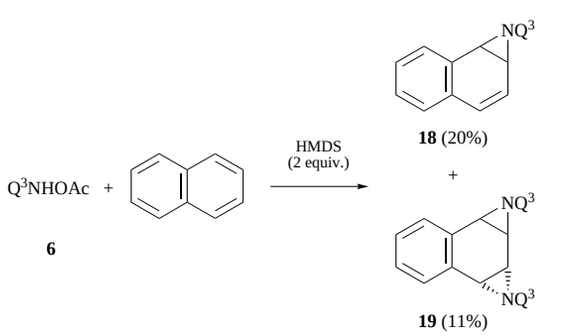
We have previously shown that yields of aziridines using 3-acetoxyamino-2-alkylquinazolinones can also be increased by the presence of trifluoroacetic acid (TFA) in the reaction mixture.‡[,6] In fact reaction of Q^2NHOAc **5** with allyl chloride (1.5 equiv.) under these conditions gave a 91% yield of aziridine **13**. However, the lack of stability of the alkene or the aziridine product to TFA means that the above method cannot be used in many cases. Thus styrene undergoes polymerisation at the concentration of TFA used, faster than it undergoes aziridination. In the aziridination in Scheme 5 using Q^4NHOAc **16**,



16 Q^4NHOAc **17**

Scheme 5

the yield of aziridine **17** is raised from 29% (using 3 equiv. of alkene) to 50% (using 1.5 equiv. of alkene and 2 equiv. of HMDS).[7] The acid sensitivity of β-trimethylsilylstyrene precludes the use of TFA in this aziridination. Aziridination of naphthalene (3 equiv.) with Q^3NHOAc **6** in the presence of HMDS gives a mixture of mono- and bis-aziridination products **18** and **19** in 20 and 11% yields respectively (Scheme 6),

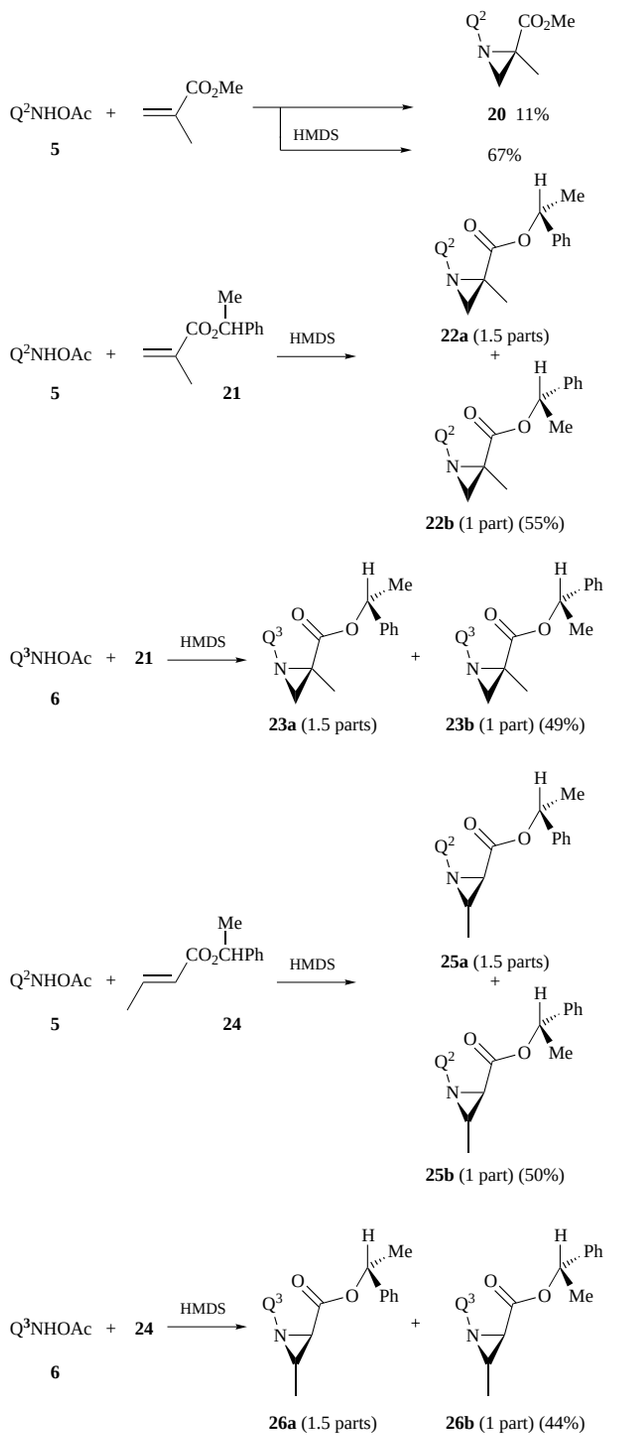


Scheme 6

after chromatographic separation. In the absence of HMDS, a 1:6 ratio of bis-aziridine **19** to 3*H*-quinazolinone **10** was obtained from NMR examination of the crude reaction product.§

Aziridination of α,β-unsaturated esters in the presence of HMDS

Although α,β-unsaturated esters and their aziridination products are stable to the TFA concentrations used in the method referred to above, comparable enhancements in isolated yields are obtained in the aziridination of these α,β-unsaturated esters with 3-acetoxyaminoquinazolinones in the presence of HMDS. Thus the yield of aziridine **20**[1] from reaction of methyl methacrylate with Q^2NHOAc **5** is raised from 11 to 67% by the addition of HMDS (2 equiv.) to the reaction mixture (Scheme 7).



Scheme 7

‡ This beneficial effect of TFA on yields of aziridines seems to contradict the conclusions drawn in this paper. However, it should be noted that this effect of TFA requires addition of 3 equiv. of the acid which, we believe, activates the 3-acetoxyaminoquinazolinone in these aziridinations by protonation at N-1 in addition to protonation on the carbonyl oxygen (see ref. 6 and S. Ulukanli, unpublished work).

§ Predominant 1,2-addition to naphthalene as in this reaction is unusual since the remaining double bond in the now non-aromatic ring is more reactive than any peripheral double bond of naphthalene.

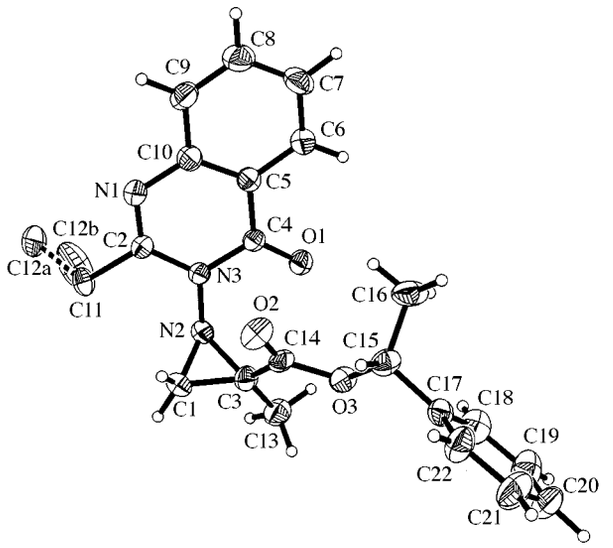


Fig. 1 The molecular structure of **22a** showing the atom numbering scheme and 30% displacement ellipsoids. Dashed bonds are drawn to the disordered sites C12a and C12b (56 : 44).

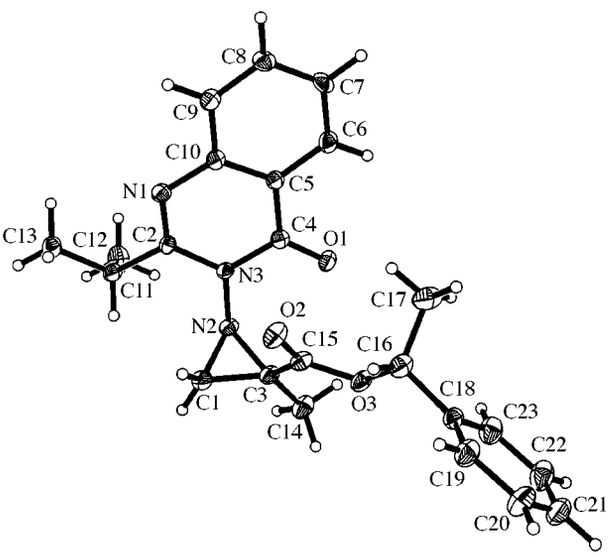


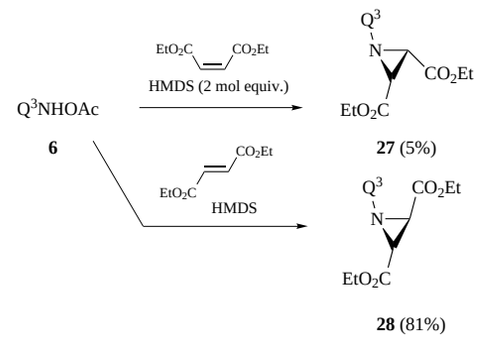
Fig. 2 The molecular structure of **23a** showing the atom numbering scheme and 30% displacement ellipsoids

We have previously shown that high or even complete diastereoselectivity in these aziridinations is obtained when the 2-substituent in the quinazolinone ring is chiral and the alkene is prochiral (*reagent-control* diastereoselectivity; see Scheme 5 and below). Esters **21** and **24**, prepared by esterification of methacrylic and crotonic acid respectively with racemic α-methylbenzyl alcohol, were aziridinated with Q^2NHOAc **5** and with Q^3NHOAc **6** for a preliminary examination of *substrate-controlled* diastereoselectivity in these aziridinations. Reaction of the chiral ester **21** with Q^2NHOAc **5** in the presence of HMDS gave aziridines **22a/22b** in a 1.5 : 1 ratio from examination of the crude mixture by NMR spectroscopy. The combined yield of **22a/22b** after chromatography was 55% and the major diastereoisomer was obtained pure by crystallisation from ethanol. Assignment of relative configuration to these diastereoisomers was possible from an X-ray crystal structure determination carried out on the major one **22a** (Fig. 1). Similar results were obtained using Q^3NHOAc **6** (Scheme 7): the same 1.5 : 1 ratio of diastereoisomers **23a/23b** was obtained (total yield 49%) with the same preferred sense of diastereoselectivity as revealed by an X-ray crystal structure determination on **23a** (Fig. 2). In the absence of HMDS in these aziridinations of ester **21** the yields of products were <15%.

Likewise, aziridination of the chiral crotonate ester **24** with Q^2NHOAc **5** and with Q^3NHOAc **6** gave acceptable yields of aziridine **25a/25b** and **26a/26b** (Scheme 7) only in the presence of HMDS. The identity in magnitude and presumably, sense of diastereoselectivity in these aziridinations using chiral esters **21** and **24** is not surprising since similar transition states are anticipated in each case: the relative configurations in the aziridine products **25a/25b** and **26a/26b** are assigned accordingly.

Stereospecificity and stereoselectivity in the reaction of Q^3NHOAc 6 with alkenes in the presence of HMDS

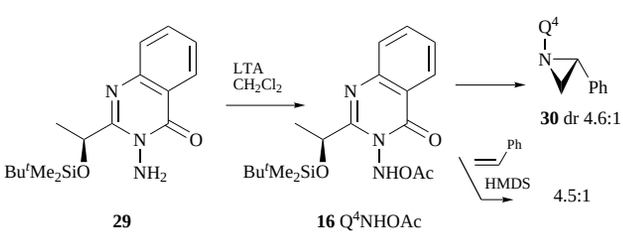
Reaction of Q^3NHOAc **6** with diethyl maleate, even in the presence of HMDS, gave the *cis*-aziridine **27** in only 5% yield (Scheme 8). Under the same conditions, reaction with diethyl



Scheme 8

fumarate gave only the *trans*-aziridine **28** (with 3 equiv. of alkene the yield of aziridine **28** is high even in the absence of HMDS). In the NMR spectrum of aziridine **28**, a chiral molecule, the two methyl groups of the isopropyl are non-equivalent whereas in the NMR spectrum of aziridine **27** they are equivalent as a result of the plane of symmetry present. Thus aziridination with Q^3NHOAc **6** in the presence of HMDS takes place stereospecifically with retention of the alkene configuration in the product. This same stereospecificity is also always observed in aziridination of alkenes using 3-acetoxyaminoquinazolinones in the absence of HMDS.[8]

Aziridination of styrene with 3-acetoxyaminoquinazolinone **16** (Q^4NHOAc) bearing an (*S*)-lactic acid derived 2-substituent, gives a 4.5 : 1 ratio of diastereoisomers of aziridine **30** (Scheme 9), a ratio indistinguishable from that obtained in the absence of HMDS.[8]

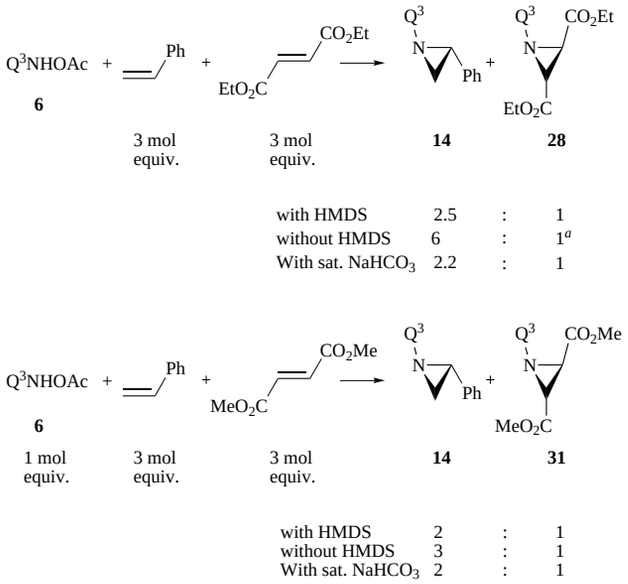


Scheme 9

Mechanism of aziridinations using 3-acetoxyaminoquinazolinones in the presence of HMDS

By analogy with the explanation offered previously for the increased yields in aziridinations using Q^1NHOAc **4** we believe that the similarly increased yields resulting from addition of HMDS can be accounted for by its (irreversible) reaction with acetic acid co-produced in the aziridination, thereby prolonging the lifetime of the aziridinating agent. The presence of HMDS did not appear to affect the nature of the aziridinating agent since stereospecificity was still obtained in reactions with *Z*- and *E*-alkenes (Scheme 8) and, more testingly, the (reagent-controlled) diastereoselectivity of the aziridination of styrene with Q^5NHOAc **16** was unaffected (Scheme 9). It was surprising to find, therefore that the selectivity of aziridination using

Q^3NHOAc **6**, in its reaction with two alkenes of very different electron demand (styrene and diethyl fumarate), *was* affected by the presence of HMDS (Scheme 10). The same relatively

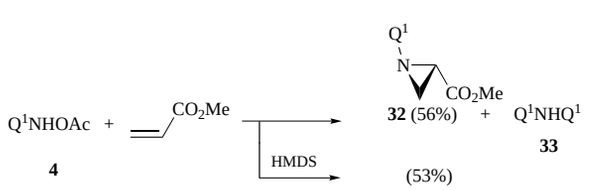


Scheme 10 [a] Previously (ref. 3) in this case we reported (in error) exclusive addition to styrene

increased reactivity of Q^3NHOAc **6** towards the electron deficient alkene was obtained using a mixture of dimethyl fumarate and styrene in the presence of HMDS.

However, this small effect of HMDS on the selectivity of the reaction of Q^3NHOAc **6** with the two alkenes in Scheme 10 does not appear to be associated specifically with HMDS since it was reproduced when these competitive aziridinations were carried out in a vigorously stirred (emulsion) mixture of dichloromethane and saturated aqueous sodium hydrogen carbonate. It is likely, therefore, that removal of acetic acid from the reaction mixture, whether by the action of HMDS or base, has a more retarding effect on the rate of aziridination of styrene than of dialkyl fumarate.¶ As expected, carrying out these aziridinations in the presence of aqueous base also raised the yield of product. Thus the highest isolated yield obtained in aziridination of hex-1-ene by Q^3NHOAc **6** in the presence of aqueous sodium hydrogen carbonate under a variety of conditions (emulsion, two phase system) was 29%.

Since the 2-trifluoromethyl substituent in Q^1NHOAc **4** is believed to stabilise this compound towards decomposition by acetic acid (see above) the beneficial effect of HMDS addition on yields in aziridinations using **4** would be expected to be less. In agreement with this expectation, reaction of methyl acrylate (2 equiv.) with Q^1NHOAc **4** gives a 56% yield of product **32**: when this reaction was carried out in the presence of HMDS a slightly lower yield of **32** (53%) was obtained, the by-product in this case is the *N*,*N*-bis(4-oxoquinazolin-3-yl)amine **33**.[2]



Scheme 11

¶ From the different mechanisms proposed for the aziridination of nucleophilic alkenes (*e.g.* styrene) and electrophilic alkenes (dialkyl fumarate) (see R. S. Atkinson, J. Fawcett, D. R. Russell and P. J. Williams, *Tetrahedron Lett.*, 1995, **36**, 3241) protonation/solvation of the acetoxy leaving group by acetic acid would be expected to be more important in aziridination of styrene.

Experimental

For general experimental details see ref. 5. All NMR spectra were run in $CDCl_3$ using trimethylsilane as internal standard for carbon at 75 MHz and for proton at the field strength indicated. *J* Values are given in Hz. Hexamethyldisilazane (HMDS) was purchased (Aldrich) and used as received.

General procedure (1) for the aziridination of alkenes

3-Aminoquinazolinone (1 mol equiv.) and acetic acid-free lead tetraacetate (LTA) (1.1 mol equiv.) were added alternately and continuously in very small portions over 15 min to a vigorously stirred solution of dry dichloromethane (1 cm^3 per 100 mg of 3-aminoquinazolinone) cooled with a dry ice–acetone bath held at −20 to −25 °C. The mixture was then stirred for a further 5 min, before dropwise addition of the alkene (1.5–3.5 mol equiv.) as a solution in dichloromethane (1 cm^3 per 500 mg) over 2 min and the temperature of the solution allowed to rise to ambient, over 20–25 min with stirring. Lead diacetate was separated, washed with dichloromethane, the organic solution washed successively with saturated aqueous sodium hydrogen carbonate and water, dried with magnesium sulfate and the solvent removed by evaporation under reduced pressure.

General procedure (2) for the aziridination of alkenes in the presence of HMDS

A solution of 3-acetoxyaminoquinazolinone at −20 °C was prepared as described above, separated from lead diacetate at this temperature (on a small scale a Pasteur pipette can be used) and the cold solution added dropwise over 2 min to a stirred solution of the alkene (1.5–3.5 mol equiv.) in dichloromethane (1 cm^3 per 500 mg) containing HMDS (2–3 mol equiv.) held at −20 °C. The temperature of the stirred solution was allowed to rise to room temp. over 20–25 min before it was diluted with dichloromethane and then washed successively with saturated aqueous sodium hydrogen carbonate and water, dried with magnesium sulfate and the solvent removed by evaporation under reduced pressure.

Aziridination of hexene

The general procedure (2) was followed using **3** (0.2 g, 0.985 mmol), LTA (0.46 g, 1.08 mmol), HMDS (0.32 g, 1.97 mmol) and hex-1-ene (0.25 g, 2.96 mmol) in dichloromethane (2 cm^3). The crude product contained a 3.5 : 1 ratio of aziridine **12** to 3*H*-quinazolinone **10** from comparison of signals at δ 3.75 and 3.08 in its NMR spectrum (see below). Flash chromatography of this crude product, eluting with light petroleum–ethyl acetate (4 : 1), gave 2-*butyl*-1-(2-*isopropyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)*aziridine* **12** (R_f 0.52) (0.2 g, 33%) as a colourless oil (Found: M^+, 285.1842. $C_{17}H_{23}N_3O$ requires *M*, 285.1841); δ_H(300 MHz) 0.98 (t, *J* 7.1, CH_2CH_3), 1.40–1.57 (11H, m, CH_3CHCH_3, 5 × C*H*), 2.18–2.24 (m, C*H*), 2.46–2.48 (m, *HCH*N), 2.84–2.91 (m, C*H*N), 3.75 (septet, *J* 6.7, CH_3CHCH_3), 7.40 [ddd, *J* 7.9, 6.6 and 1.4, 6-H (Q^3)], 7.63–7.73 [m, 7-H and 8-H (Q^3)] and 8.20 [ddd, *J* 7.9, 1.4 and 0.8, 5-H (Q^3)]; δ_C 13.87 (CH_3), 20.61, 21.26 (CH_3CHCH_3), 22.47 and 28.03 (2 × CH_2), 30.64 (CH_3CHCH_3), 30.93 and 41.34 (2 × CH_2), 46.29 (CHN), 121.10 [CCO (Q^3)], 125.87, 126.52, 126.72 and 133.28 [4 × CH (Q^3)], 146.05 [CN=C (Q^3)], 160.05 [C=N (Q^3)] and 161.09 [CO (Q^3)]; ν_{max}/cm^{-1} 1730w, 1670s and 1590s; *m*/*z* 285 (M^+, 59%), 242 (21), 214 (62), 189 (51), 188 (40), 187 (42), 173 (100), 160 (29), 145 (29), 130 (41) and 98 (32).

Aziridination of allyl chloride

The general procedure (2) was followed using **3** (0.5 g, 2.46 mmol), LTA (1.15 g, 2.59 mol), HMDS (0.8 g, 4.93 mmol) and allyl chloride (0.57 g, 7.39 mmol) in dry dichloromethane (5 cm^3). After work up, the residue was purified by flash chromatography over silica with light petroleum–ethyl acetate (5 : 1) as eluent. The 2-(*chloromethyl*)-1-(2-*isopropyl*-4-*oxo*-3,4-*dihydro*-

quinazolin-3-*yl*)*aziridine* **15** (R_f 0.34) was obtained as a pale yellow oil (0.23 g, 18%) (Found: M^+, 277.0981. $C_{14}H_{16}N_3OCl$ requires *M*, 277.0982); δ_H(250 MHz) 1.55 and 1.60 (2 × d, *J* 6.7, CH_3CHCH_3), 2.73 (dd, *J* 5.1 and 1.5, azir. 3-H *cis* to CH_2Cl), 3.02 (dd, *J* 7.4 and 1.5, azir. 3-H *trans* to CH_2Cl), 3.67 (dddd, *J* 7.4, 6.8, 5.1 and 4.8, $CHCH_2Cl$), 3.78 (dd, *J* 11.2 and 6.8, CHHCl), 3.88 (septet, *J* 6.7, CH_3CHCH_3), 4.28 (dd, *J* 11.2 and 4.8, CHHCl), 7.58 [ddd, *J* 7.9, 7.6 and 1.1, 6-H (Q^3)], 7.78–7.87 [m, 7-H and 8-H (Q^3)] and 8.31 [dd, *J* 7.9 and 1.1, 5-H (Q^3)]; δ_C 21.0 and 21.8 (CH_3CHCH_3), 31.3 (CH_3CHCH_3), 39.6 (CH_2), 44.0 (CHN), 44.6 (CH_2Cl), 121.6 [CCO (Q^3)], 126.4, 126.7, 127.5 and 134.2 [4 × CH (Q^3)], 146.6 [CN=C (Q^3)] and 161.0 and 161.6 [C=N (Q^3), CO (Q^3)]; ν_{max}/cm^{-1} 1760m, 1680s, 1610s and 1600s; *m*/*z* 277 (M^+, 52%), 242 (44), 214 (30), 184 (24), 173 (64), 146 (25), 145 (100), 144 (23), 130 (83), 104 (20), 103 (34), 90 (28), 77 (20) and 76 (46).

Aziridination of styrene

The general procedure (2) was followed using **3** (0.3 g, 1.48 mmol), LTA (0.721 g, 1.63 mmol), HMDS (0.478 g, 2.96 mmol) and styrene (0.154 g, 1.48 mmol) in dry dichloromethane (5 cm^3). The crude product mixture (0.322 g) contained aziridine **14** (66%) and Q^3H **10** in an 8.86:1 ratio from signals in its NMR spectrum at δ 8.14 and 8.2 respectively.

The same reaction carried out according to the general procedure (1), gave aziridine **14** (56%) from comparison of the same signals in the NMR spectrum of the crude reaction product.

Aziridination of naphthalene

The general procedure (2) was followed using **3** (0.5 g, 2.46 mmol), LTA (1.15 g, 2.59 mol), HMDS (0.8 g, 4.93 mmol) and naphthalene (0.95 g, 7.39 mmol) in dry dichloromethane (5 cm^3). After work up, the residue was purified by flash chromatography over silica previously washed with a triethylamine solution (1% in light petroleum–ethyl acetate) eluting with light petroleum–ethyl acetate (6:1) and 1-(2-*isopropyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)-1a,7b-*dihydro*-1H-*naphtho*[1,2-b]*azirine* **18** (R_f 0.25) was obtained as colourless solid (0.16 g, 20%), mp 113–115 °C (Found: M^+, 329.1528. $C_{21}H_{19}N_3O$ requires *M*, 329.1528); δ_H(250 MHz) 1.46 and 1.50 (2 × d, *J* 6.7, CH_3CHCH_3), 3.75 (septet, *J* 6.7, CH_3CHCH_3), 3.86 (dd, *J* 7.5 and 4.6, NCHCH=CH), 4.41 (d, *J* 7.5, NCH), 6.55 (dd, *J* 9.6 and 4.6, NCHCH=CH), 6.78 (d, *J* 9.6, NCHCH=CH), 7.25–7.37 (1H), 7.39–7.58 (3H), 7.68–7.80 (2H) and 7.83–7.90 (1H) [4 × m, 4 × CH (Ar) 3 × CH (Q^3)] and 8.32 [1H, dd, *J* 7 and 0.9, 5-H (Q^3)]; δ_C 21.5 and 21.6 (2 × CH_3), 31.5 (CH_3CHCH_3), 50.8 and 53.2 (2 × NCH), 121.0 and 121.1 (2 × CH), 121.7 [CCO (Q^3)], 126.4, 126.7, 126.9 and 127.2 (4 × CH), 127.4 (C), 129.2 (CH), 129.5 (C), 130.5, 132.6 and 135.0 (3 × CH), 146.7 [CN=C(Q^3)] and 160.4 and 162.0 [C=N (Q^3), CO (Q^3)]; ν_{max}/cm^{-1} 1675s, 1610m and 1590s; *m*/*z* 329 (M^+, 61%), 187 (41), 145 (21), 143 (44), 142 (69), 141 (38), 130 (34), 128 (100), 115 (32) and 76 (24).

Further elution with the same solvent mixture the 1,2-*bis*-(2-*isopropyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)-1,1a,1b,2,2a,6b-*hexahydronaphtho*[1,2-b:3,4-b′]*bis*(*azirine*) **19** (R_f 0.14) as a colourless oil (0.074 g, 11%) (Found: M^+, 530.2431. $C_{32}H_{30}N_6O_2$ requires *M*, 530.2430); δ_H(250 MHz) 1.28 and 1.32 (2 × d, *J* 6.7, CH_3CHCH_3), 3.59 (septet, *J* 6.7, 2 × CH_3CHCH_3), 3.74 (d, *J* 8.3, 2 × NCH), 4.18 (d, *J* 8.3, 2 × NCHAr), 7.28–7.39 [m, 4 × CH (Ar)], 7.52–7.69 [m, 6 × CH (Ar)], 8.11–8.27 [m, 2 × CH (Ar)]; δ_C 21.5 and 21.6 (4 × CH_3), 31.6 (2 × CH_3CHCH_3), 46.6 and 47.8 (4 × NCH), 121.6 [2 × CCO (Q^3)], 126.7, 126.8, 127.5 and 129.7 (8 × CH), 130.8 (2 × C), 131.6 and 134.8 (4 × CH), 146.6 [2 × CN=C (Q^3)] and 160.6 and 161.3 [2 × C=N (Q^3), 2 × CO (Q^3)]; ν_{max}/cm^{-1} 1680s, 1610m and 1595s; *m*/*z* (CI) 531 (M + 1). When this experiment was repeated in the absence of HMDS, a 1:6 ratio of bis-aziridine **19**:2-isopropylquinazolinone **10** was isolated from comparison of signals at δ 3.75 (for **19**) and 3.08 (for **10**).

Aziridination of methyl methacrylate using Q^2NHOAc 5 in the presence of HMDS

The general procedure (2) was followed using **2** (300 mg, 1.59 mmol), LTA (774 mg, 1.75 mmol), methyl methacrylate (239 mg, 2.385 mmol) and HMDS (513 mg, 3.18 mmol) in dichloromethane (4 cm^3) to give *methyl* 1-(2-*ethyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)-2-*methylaziridine*-2-*carboxylate* **20** as a colourless oil (306 mg, 67%) after chromatography and eluting with light petroleum–ethyl acetate (1:1) (R_f 0.53). The product was crystallised on addition of ethanol as a colourless solid, mp 90–93 °C (from ethanol) (Found: C, 62.7; H, 6.0; N, 14.6. $C_{15}H_{17}N_3O_3$ requires C, 62.7; H, 5.95; N, 14.6%); δ_H(250 MHz) 2:1 ratio of invertomers (major *N*-invertomer) 1.43 (t, *J* 7.5, CH_2CH_3), 1.79 (s, azir. Me), 2.84 (d, *J* 1.1, azir. HHC *trans* to Q^2), 2.98 (m, *J* 7.5, CH_2CH_3), 3.29 (dd, *J* 1.1, azir. HHC *cis* to Q^2), 3.55 (s, OMe), 7.83–7.56 [m, 6-H, 7-H, 8-H (Q^2)] and 8.20 [d, *J* 8.2, 5-H (Q^2)]; signals from the minor *N*-invertomer are visible at δ ~1.40 (s, t, *J* 7.5, CH_2CH_3 and azir. Me), 2.78 (m, *J* 7.5, CH_2CH_3) and 3.83 (s, OMe); ν_{max}/cm^{-1} 1730s, 1665s and 1595s.

Aziridination of α-methylbenzyl methacrylate 21 using Q^2NHOAc 5 in the presence of HMDS

The general procedure (2) was followed using **2** (200 mg, 1.05 mmol), LTA (517 mg, 1.16 mmol), the methacrylate **21** (401 mg, 2.11 mmol) and HMDS (341 mg, 2.11 mmol) in dichloromethane (4 cm^3) to give α-*methylbenzyl* 1-(2-*ethyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)-2-*methylaziridine*-2-*carboxylate* **22a**/**22b** as an oil (254 mg, 61.5%) (R_f 0.37) after chromatography over silica and eluting with light petroleum–ethyl acetate (3:1). From its NMR spectrum, this aziridine comprised two diastereoisomers in a 1.5:1 ratio from comparison of signals at δ 8.32 and 8.16. The major *aziridine* diastereoisomer **22a** crystallised on addition of ethanol as a colourless solid, mp 114.5–116 °C (from ethanol) (Found: C, 69.7; H, 6.2; N, 11.1. $C_{22}H_{23}N_3O_3$ requires C, 70.0; H, 6.15; N, 11.15%); δ_H(250 MHz) 1.32 (t, *J* 7.6, CH_2CH_3), 1.53 (d, *J* 6.9, OCHPhCH_3), 1.91 (s, azir. Me), 3.05 (m, CH_2CH_3, and azir. HHC *trans* to Q^2), 3.48 (br s, azir. HHC *cis* to Q^2), 6.1 (q, *J* 6.9, OCHPhMe), 7.31 (m, C_6H_5), 7.48 [d, *J* 7.6, H-6 (Q^2)], 7.8–7.73 [m, H-7 and H-8 (Q^2)] and 8.32 [d, *J* 7.6, H-5 (Q^2)]; *m*/*z* 377 (M^+, 49%), 200 (38), 174 (38), 131 (55) and 105 (100). A crystal of aziridine **22a** suitable for X-ray crystallography was prepared by crystallisation from ethanol. A signal from the minor diastereoisomer **22b** was visible at δ 8.16 [d, *J* 7.6, H-5 (Q^2)] in the crude reaction product.

Aziridination of α-methylbenzyl methacrylate 21 using Q^3NHOAc 6 in the presence of HMDS

The general procedure (2) was followed using **3** (400 mg, 1.97 mmol), LTA (961 mg, 2.16 mmol), the methacrylate **21** (1.12 g, 5.91 mmol) and HMDS (952 mg, 5.91 mmol) in dichloromethane (6 cm^3) to give **23a**/**23b** after chromatography over silica and eluting with light petroleum–ethyl acetate (4:1) as an oil (R_f 0.28) (319 mg, 50%) containing a 1.5:1 ratio of diastereoisomers from the signals at δ 8.09 and 7.97 in its NMR spectrum. The major α-*methylbenzyl* 1-(2-*isopropyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)-2-*methylaziridine*-2-*carboxylate* diastereoisomer **23a** crystallised on addition of ethanol as a colourless solid (379 mg, 49%), mp 133–134 °C (from ethanol) (Found: C, 70.3; H, 6.5; N, 10.6. $C_{23}H_{25}N_3O_3$ requires C, 70.55; H, 6.45; N, 10.75%); δ_H(250 MHz) 1.1 (d, *J* 7.5, CH_3CHCH_3), 1.22 (d, *J* 7.5, CH_3CHCH_3), 1.3 (d, *J* 6.6, OCHPhCH_3), 1.65 (s, azir. ring Me), 3.14 (d, *J* 1.3, azir. HHC *trans* to Q^3), 3.24 (CH_3CHCH_3), 3.35 (d, *J* 1.3, azir. HHC *cis* to Q^3), 5.8 (q, *J* 6.6, OCHPhCH_3), 7.1 (m, C_6H_5), 7.2 [ddd, *J* 9.8, 7.9 and 1, H-6 (Q^3)], 7.5–7.39 [m, H-7 and H-8 (Q^3)] and 8.09 [dd, *J* 7.9 and 1.0, H-5 (Q^3)]; *m*/*z* 391 (M^+, 53%), 214 (36), 173 (27), 145 (43), 130 (40) and 105 (100). A crystal of aziridine **23a** suitable for X-ray crystallography was prepared by crystallisation from ethanol. A signal from the minor diastereoisomer **23b** was

visible at δ 7.97 [dd, *J* 7.9 and 1.0, H-5 (Q)] in the crude reaction product.

Aziridination of α-methylbenzyl crotonate 24 using Q^2NHOAc 5 in the presence of HMDS

The general procedure (2) was followed using **2** (300 mg, 1.58 mmol), LTA (777 mg, 1.75 mmol), the title crotonate (604 mg, 3.18 mmol) and HMDS (517 mg, 3.17 mmol) in dichloromethane (4 cm^3). After chromatography over silica and eluting with light petroleum–ethyl acetate (4:1), an NMR spectrum of the combined and evaporated fractions (R_f 0.35) (0.3 g, 50%) showed the presence of two diastereoisomers of aziridine **25a/25b** in a 1.5:1 ratio from signals at δ 8.2 and 8.12. The major α-*methylbenzyl* 1-(2-*ethyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)-3-*methylaziridine*-2-*carboxylate* diastereoisomer crystallised on addition of ethanol, mp 116–117 °C (from ethanol) (Found: C, 69.75; H, 6.25; N, 11.0. $C_{22}H_{23}N_3O_3$ requires C, 70.0; H, 6.15; N, 11.15%); δ_H(300 MHz) 1.44 (t, *J* 7.2, CH_2CH_3), 1.54 (d, *J* 6.6, azir. ring Me), 1.61 (d, *J* 6.5, $OCCH_3PhH$), 3.01 (dq, *J* 14.5 and 7.2, CH_2CH_3), 3.27 (d, *J* 4.8, azir. H-2), 3.48 (m, azir. H-3), 5.79 (q, *J* 6.5, $OCPhHCH_3$), 7.23 (m, C_6H_5), 7.76–7.47 [m, H-6, H-7, H-8 (Q^2)] and 8.2 [dd, *J* 8.2 and 1.1, H-5 (Q^2)]; *m*/*z* 377 (M^+, 57%), 228 (47), 174 (51), 131 (69), 105 (100) and 69 (21); signals from the minor diastereoisomer are visible at δ 3.2 (d, *J* 4.8, azir. H-2), 3.61 (m, azir. H-3) and 8.12 [d, *J* 8.2, H-5 (Q^2)].

Aziridination of α-methylbenzyl crotonate 24 using Q^3NHOAc 6 in the presence of HMDS

The general procedure (2) was followed using **3** (200 mg, 0.98 mmol), LTA (479 mg, 1.08 mmol), the crotonate **24** (373 mg, 1.97 mmol) and HMDS (317 mg, 1.97 mmol) in dichloromethane (4 cm^3). After chromatography over silica and eluting with light petroleum–ethyl acetate (3:1), a mixture of diastereoisomers **26a/26b** (R_f 0.3) was obtained as an oil (170 mg, 44%) in a 1.5:1 ratio from signals at δ 8.13 and 8.08; the major α-*methylbenzyl* 1-(2-*isopropyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)-3-*methylaziridine*-2-*carboxylate* diastereoisomer **26a** crystallised on addition of ethanol, mp 120–122 °C (Found: M^+, 391.189. $C_{22}H_{25}N_3O_3$ requires *M*, 391.189); δ_H(300 MHz) 1.25 [2 × d, *J* 7.1, $HC(CH_3)_2$], 1.36 (d, *J* 6.8, azir. Me), 1.64 (d, *J* 6.5, $OCHPhCH_3$), 3.21 (d, *J* 5.1, azir. H-2), 3.38 (m, *J* 7.1, $CHMe_2$), 3.46 (m, azir. H-3), 5.73 (q, *J* 6.5, $OCHPhCH_3$), 7.28 (m, C_6H_5), 7.4 [d, *J* 7.7, H-6 (Q^3)], 7.65–7.59 [m, H-7 and H-8 (Q^3)] and 8.13 [dd, *J* 1 and 6.5, H-5 (Q^3)]; *m*/*z* 391 (M^+, 74%), 242 (58), 188 (25), 173 (59), 145 (79), 130 (42) and 105 (100); signals from the minor diastereoisomer are visible at δ 8.08 [d, *J* 6.5, H-5 (Q^3)], 3.59 (m, azir. H-3), 3.31 (m, *J* 7.1, $CHMe_2$) and 3.08 (d, *J* 5.1, azir. H-2).

Aziridination of methyl acrylate using Q^1NHOAc 4 in the presence of HMDS

The general procedure (2) was followed using **1** (200 mg, 0.87 mmol), LTA (426 mg, 0.96 mmol), methyl acrylate (150 mg, 1.74 mmol) and HMDS (281 mg, 1.74 mmol) in dichloromethane (3 cm^3) to give a product mixture (193 mg) of aziridine **32** and Q^1NHQ^1 **33** in a 3.8:1 ratio from signals in its NMR spectrum at δ 3.93 and 10.05 respectively. The *methyl* 1-(4-*oxo*-2-*trifluoromethyl*-3,4-*dihydroquinazolin*-3-*yl*)*aziridine*-2-*carboxylate* **32** crystallised on addition of ethanol to give a colourless solid (146 mg, 53%), mp 105–107 °C (from ethanol) (Found: M^+, 313.067. $C_{13}H_{10}F_3N_3O_3$ requires *M*, 313.067); δ_H(250 MHz) 2.63 (d, *J* 4.4, azir. H-3 *trans* to Q^1), 3.74 (s, OMe), 3.93 (d, *J* 7.2, azir. H-3 *cis* to Q^1), 4.26 (dd, *J* 4.4 and 7.2, azir. H-2), 7.81–7.52 [m, 6-H, 7-H, 8-H (Q^1)] and 8.13 [dd, *J* 7.9 and 1, 5-H (Q^1)]; *m*/*z* 313 (M^+, 62%), 214 (100), 171 (27), 145 (46), 104 (88), 90 (39), 76 (51) and 55 (27); ν_{max}/cm^{-1} 1750s, 1690s and 1605m; the same experiment repeated in the absence of HMDS gave a mixture of **32** and **33** (5.8:1, 192 mg) from which *aziridine* **32** (154 mg, 56%) was obtained by crystallisation.

Aziridination of diethyl maleate

The general procedure (2) was followed using **3** (0.2 g, 0.985 mmol), LTA (0.46 g, 1.08 mmol), HMDS (0.32 g, 1.97 mmol) and diethyl maleate (0.51 g, 2.96 mmol) in dry dichloromethane (2 cm^3). Flash chromatography of the crude product over silica with light petroleum–ethyl acetate (3:1) as eluent gave *diethyl* 1-(2-*isopropyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)*aziridine*-2,3-*dicarboxylate* **27** (R_f 0.52) as a colourless oil (0.02 g, 5%) (Found: M^+, 373.1638. $C_{19}H_{23}N_3O_5$ requires *M*, 373.1638); δ_H(250 MHz) 1.24 (t, *J* 7.2, 2 × CH_3CH_2), 1.34 (d, *J* 6.8, CH_3CHCH_3), 3.97 (septet, *J* 6.8, CH_3CHCH_3), 4.18 (q, *J* 7.2, 2 × CH_3CH_2), 4.78 (s, 2 × $CHCO_2Et$), 7.33 [ddd, *J* 7.9, 6.9 and 1.4, 6-H (Q^3)], 7.55–7.70 [m, 7-H, 8-H (Q^3)] and 8.03 [dd, *J* 7.9 and 1.4, 5-H (Q^3)]; δ_C 14.5 and 21.4 (4 × CH_3), 31.6 and 41.3 (2 × CH), 62.2 (2 × CH_2CH_3), 121.8 [CCO (Q^3)], 126.5, 126.9, 127.7 and 134.9 [4 × CH (Q^3)], 146.8 [CN=C (Q^3)], 162.5 and 163.7 [C=N (Q^3) and CO (Q^3)] and 166.6 (2 × $CO_2CH_2CH_3$); ν_{max}/cm^{-1} 1730s, 1670w and 1600m; *m*/*z* 373 (M^+, 21%), 300 (60), 188 (22), 187 (23), 173 (60), 149 (30), 145 (100), 130 (57), 129 (20), 103 (23), 85 (21), 76 (23), 73 (26), 71 (24), 69 (48), 60 (23), 57 (48) and 55 (49).

Aziridination of diethyl fumarate

The general procedure (1) was followed using **3** (1.2 g, 5.9 mmol), LTA (2.77 g, 6.26 mmol) and diethyl fumarate (3.05 g, 18 mmol) in dry dichloromethane (12 cm^3). Flash chromatography of the crude product over silica and eluting with light petroleum–ethyl acetate 4:1 gave *diethyl* 1-(2-*isopropyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)*aziridine*-2,3-*dicarboxylate* **28** (R_f 0.23) as a colourless oil (1.79 g, 81%) (Found: M^+, 373.1644. $C_{19}H_{23}N_3O_5$ requires *M*, 373.1637); δ_H(300 MHz) 1.15 (t, *J* 7.2, CH_3CH_2), 1.38 (t, *J* 7.2, CH_3CH_2), 1.42 (2 × d, *J* 6.6, CH_3CHCH_3), 3.39 (septet, *J* 6.6, CH_3CHCH_3), 3.80 (d, *J* 4.6, azir. H *trans* to Q^3), 4.08 (d, *J* 4.6, azir. H *cis* to Q^3), 4.10 (q, *J* 7.2, CH_3CH_2), 4.35 (q, *J* 7.2, CH_3CH_2), 7.40 [ddd, *J* 7.9, 6.8 and 1.5, 6-H (Q^3)], 7.61–7.71 [m, 7-H and 8-H (Q^3)] and 8.16 [dd, *J* 7.9 and 1.4, 5-H (Q^3)]; δ_C 13.62 and 13.88 (2 × CH_3CH_2), 19.95 and 21.14 (CH_3CHCH_3), 30.73 (CH_3CHCH_3), 46.72 and 49.00 (2 × azir. CH), 62.29 and 62.38 (2 × CH_3CH_2), 120.70 [CCO (Q^3)], 126.08, 126.21, 127.00 and 133.64 [4 × CH (Q^3)], 145.91 [CN=C (Q^3)], 158.77 [C=N (Q^3)], 159.59 [CO (Q^3)] and 164.35 and 166.08 (2 × CO_2Et); ν_{max}/cm^{-1} 1735s, 1675s and 1571m; *m*/*z* 373 (M^+, 38%), 300 (98), 188 (47), 187 (31), 173 (100), 145 (72), 130 (41), 127 (59), 126 (21), 99 (41), 93 (30) and 84 (24).

Aziridination of dimethyl fumarate

The general procedure (1) was followed using **3** (0.3 g, 1.48 mmol), LTA (0.721 g, 1.63 mmol) and dimethyl fumarate (0.426 g, 2.93 mmol) in dry dichloromethane (4 cm^3). Trituration of the crude product with cold light petroleum to remove excess fumarate, gave a mixture of *dimethyl* 1-(2-*isopropyl*-4-*oxo*-3,4-*dihydroquinazolin*-3-*yl*)*aziridine*-2,3-*dicarboxylate* **31** and Q^3H **10** in a 3:1 ratio. The pure aziridine separated as a colourless solid (0.34 g, 66%), mp 80–82 °C (from ethanol) Found: C, 58.95; H, 5.6; N, 12.1. $C_{17}H_{19}N_3O_5$ requires C, 59.1; H, 5.55; N, 12.15%); δ_H(250 MHz) 1.27 (d, *J* 6.6, CH_3CHCH_3), 1.33 (d, *J* 6.6, CH_3CHCH_3), 3.29 (septet, *J* 6.6, CH_3CHCH_3), 3.61 (s, OMe *cis* to Q^3), 3.74 (d, *J* 4.4, azir. H *trans* to Q^3), 3.84 (s, OMe *trans* to Q^3), 4.05 (d, *J* 4.4, azir. H *cis* to Q^3), 7.65–7.31 [m, 6-H, 7-H and 8-H (Q^3)] and 8.10 [dd, *J* 7.9 and 1, 5-H (Q^3)]; *m*/*z* 345 (M^+, 36%), 286 (78), 198 (9), 187 (20), 173 (56), 145 (100), 130 (64), 105 (35), 84 (85) and 51 (34).

Competitive aziridination of styrene and diethyl fumarate in the presence of HMDS

The general procedure **2** was followed using **3** (0.2 g, 0.985 mmol), LTA (0.46 g, 1.03 mmol), HMDS (0.32 g, 2.96 mmol), styrene (0.31 g, 2.96 mmol) and diethyl fumarate (0.43 g, 2.96 mmol) in dichloromethane (2 cm^3). After work up the ratio of aziridines **14** and **28**, from integration of signals at δ 3.39 and

3.21 respectively in the NMR spectrum of the crude reaction product, was 2.5:1. When this procedure was repeated in the absence of HMDS [procedure (1)], the corresponding ratio of aziridines obtained was 6:1 from comparison of same signals.

Competitive aziridination of styrene and dimethyl fumarate in the presence of HMDS

The general procedure **2** was followed using **3** (0.2 g, 0.985 mmol), LTA (0.48 g, 1.08 mmol), HMDS (0.32 g, 2.96 mmol), styrene (0.31 g, 2.96 mmol) and dimethyl fumarate (0.51 g, 2.96 mmol) in dichloromethane (3 cm^3). After work up the ratio of aziridines **14** and **31**, from integration of signals at δ 4.05 and 3.21 respectively in the NMR spectrum of the crude reaction product, was 2:1. When this procedure was repeated in the absence of HMDS [procedure (1)], the ratio of aziridines obtained was 3:1.

Competitive aziridination of styrene and diethyl fumarate in the presence of saturated aqueous sodium hydrogen carbonate

The experiment above was repeated using the general procedure (1) but the dichloromethane solution, after separation from the lead diacetate, was added to vigorously stirred saturated aqueous sodium hydrogen carbonate (2 cm^3) at 0 °C followed immediately by the styrene and diethyl fumarate. The temperature was allowed to rise to ambient over 30 min with stirring sufficient to maintain an emulsion. Further dichloromethane (10 cm^3) was then added, the dichloromethane separated, washed with water, dried and evaporated under reduced pressure. The ratio of aziridines **14** and **28** present from NMR spectrum of the crude reaction product was 2.2:1 by comparison of the signals referred to above.

The same experiment was also repeated using dimethyl fumarate instead of diethyl fumarate and examination of the NMR spectrum of the crude mixture showed 2:1 ratio of aziridines **14** and **31**.

Aziridination of hexene in the presence of saturated aqueous hydrogen carbonate. The experiment above was repeated but with addition of hex-1-ene (0.2 g, 0.985 mmol) instead of styrene–dialkyl fumarate. After the same work up, aziridine **12** (0.082 g, 29%) was isolated from the crude product after chromatography over silica using the same conditions described earlier.

X-Ray crystallography data for 22a

$C_{22}H_{23}N_3O_3$, $M = 377.44$, monoclinic, space group $P2_1/c$, $a = 22.254(3)$, $b = 9.020(1)$, $c = 10.132(1)$ Å, $\beta = 96.73(1)°$, $V = 2019.8(4)$ Å^3 (by least squares refinement on diffractometer angles for 32 centred reflections in the range $2.5 < \theta < 12.5°$), $Z = 4$, $D_c = 1.242$ Mg m^{-3}, μ(Mo-Kα) = 0.079 mm^{-1} colourless block (from ethanol), crystal dimensions 0.48 × 0.46 × 0.40 mm.

Data collection and processing. Data were measured on a Siemens P4 diffractometer at 190 K using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) using an ω scan technique. Three standard reflections monitored every 100 scans showed no significant variation in intensity, the reflections were corrected for Lorentz and polarisation effects. 4442 data were measured ($2.6 < \theta < 25.0°$), with 3277 independent reflections (merging $R_{int} = 0.047$) and 3270 having $I > 2\sigma(I)$ regarded as observed.

Structure solution and refinement. The structures were solved by direct methods using the program SHELXTL-PC[9] and refined by full-matrix least-squares on F^2 using the program SHELXL93.[10] The terminal atom of the ethyl group was refined as disordered between two sites C12a and C12b with site occupancies of 0.56 and 0.44 respectively. All hydrogen atoms were included in calculated positions (C–H = 0.96 Å) using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares based on F^2 gave $R1 = 0.072$, $wR2 = 0.269$ for all data, for 262 parameters (R factors defined in ref. 2), weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.096P)^2 + 1.63P]$ where $P = [max(F_o^2, 0) + 2F_c^2]/3$, GOF = 1.043, maximum $\Delta/\sigma = 0.021$, maximum $\Delta\rho = 0.290$ e Å^{-3}.

X-Ray crystallographic data for 23a

$C_{23}H_{25}N_3O_3$, $M = 391.46$, monoclinic, space group $P2_1/c$, $a = 22.406(4)$, $b = 9.024(2)$, $c = 10.263(3)$ Å, $\beta = 98.16(1)°$, $V = 2054.1(8)$ Å^3 (by least-squares refinement on diffractometer angles for 29 centred reflections in the range $2.5 < \theta < 12.5°$), $Z = 4$, $D_c = 1.266$ Mg m^{-3}, μ(Mo-Kα) = 0.085 mm^{-1} colourless block (from ethanol), crystal dimensions 0.52 × 0.40 × 0.08 mm.

Data collection and processing. Data were collected and processed as for **22a**. 3727 data were measured ($2.5 < \theta < 23.0°$), with 2729 independent reflections (merging $R_{int} = 0.054$) and 2729 having $I > 2\sigma(I)$.

Structure solution and refinement. The structures were solved using the same method as **22a**, except that the phenyl group C18 to C23 was refined as rigid group. Full-matrix least-squares based on F^2 gave $R1 = 0.062$, $wR2 = 0.174$ for all data, for 250 parameters, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.089P)^2 + 0.46P]$ where $P = [max(F_o^2, 0) + 2F_c^2]/3$, GOF = 1.021, maximum $\Delta/\sigma = 0.016$, maximum $\Delta\rho = 0.220$ e Å^{-3}.

Full crystallographic details for **22a** and **23a**, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web pages (http://chemistry.rsc.org/rsc/p1pifa.htm). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/175.

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