PERKIN 1

Aziridination of cyclic dienes with enantiopure 3-acetoxyamino-quinazolin-4(3*H*)-ones

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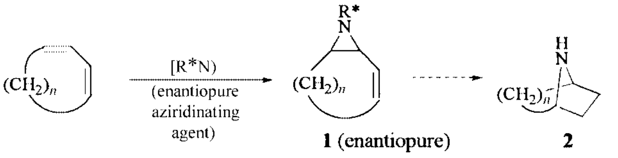
Received (in Cambridge, UK) 20th March 2001, Accepted 15th May 2001
First published as an Advance Article on the web 4th June 2001

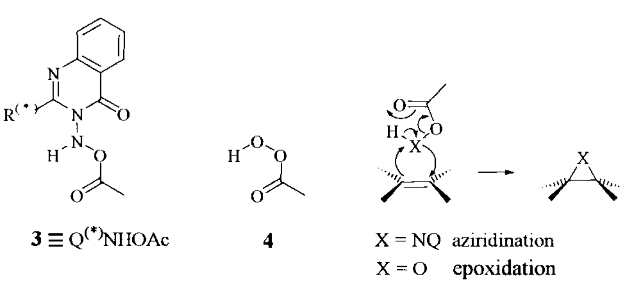
Aziridination of cyclopentadiene and cyclohepta-1,3-diene with (*S*)-3-acetoxyamino-2-(3-hydroxy-2,2-dimethylpropyl)quinazolin-4(3*H*)-one **6** (Q^{1}NHOAc) in the presence of titanium(IV) *tert*-butoxide in dichloromethane takes place highly diastereoselectively: X-ray structure determinations show that the preferred sense of diastereoselectivity in both cases is the same as that previously found for aziridination of butadiene with **6**. Aziridination of cyclohexa-1,3-diene with **6** was less diastereoselective in dichloromethane solution but highly diastereoselective in acetonitrile: in this solvent two diastereoisomeric *cis*-4-(Q^1-amino)cyclohexen-3-ols **27** and **28** were also obtained as by-products. The same two amino alcohols were obtained by ring-opening of the aziridine with acid and were each converted into Q^1-free oxazolidinones having optical rotations which were similar in magnitude but opposite in sign.

Enantiopure cyclic vinylaziridines **1** are potentially useful relay compounds for the synthesis of a range of 1,2,3,4-tetra-substituted cyclic amine derivatives of defined configuration and (n + 1)-azabicyclo[n.1.0] derivatives **2** by vinylaziridine–pyrroline rearrangement.[1] Because of the dearth of methods for stereoselective aziridination,[2,3] the most direct route to these compounds **1** from the corresponding dienes (Scheme 1) has not been explored. Consequently, presently available methods for synthesis of enantiopure **1** start with enantiopure dienes (substrate-controlled diastereoselectivity) and are therefore less general.[4]



Scheme 1

3-Acetoxyaminoquinazolinones **3** (QNHOAc) convert alkenes into aziridines in a reaction which resembles the conversion of alkenes into epoxides by peroxyacetic acid **4** (Scheme 2).[2] In both cases, 3-membered ring formation takes place stereospecifically with retention of alkene configuration in the product. However, one advantage in the use of QNHOAc **3** is that high or complete diastereoselectivity is possible using prochiral alkenes when the R group is chiral (R*) (reagent-controlled diastereoselectivity).



Scheme 2

Thus Q^{1}NHOAc **6**, prepared *in situ* by *N*-acetoxylation of the (*S*)-*tert*-leucine-derived **5** using lead tetraacetate (LTA), aziridinates *e.g.* butadiene or styrene highly diastereoselectively in the presence of titanium(IV) *tert*-butoxide (TTB) *via* a transition state (TS$^\#$) geometry believed to resemble that in **7** (Scheme 3).[5]

endo-Overlap of the conjugated double bond in butadiene/styrene with Q^1 leads to *cis*-1,2-disubstituted aziridines **8a** or **9a** as the kinetically-formed products: these then spontaneously *N*-invert to the more stable *trans*-1,2-disubstituted **8b** or **9b**.

The value of these aziridines lies in their potential for conversion to Q^1-free chirons by aziridine ring-opening and Q^1–N bond cleavage. Thus the styrene-derived aziridine **9b** has been converted into either of the Boc-protected 1,2-diamines **10** and **enant. 10** (Scheme 4).[6]

The high diastereoselectivity obtained in the aziridination of butadiene using Q^{1}NHOAc **6** in the presence of TTB encouraged us to examine its use in aziridination of cyclic dienes.

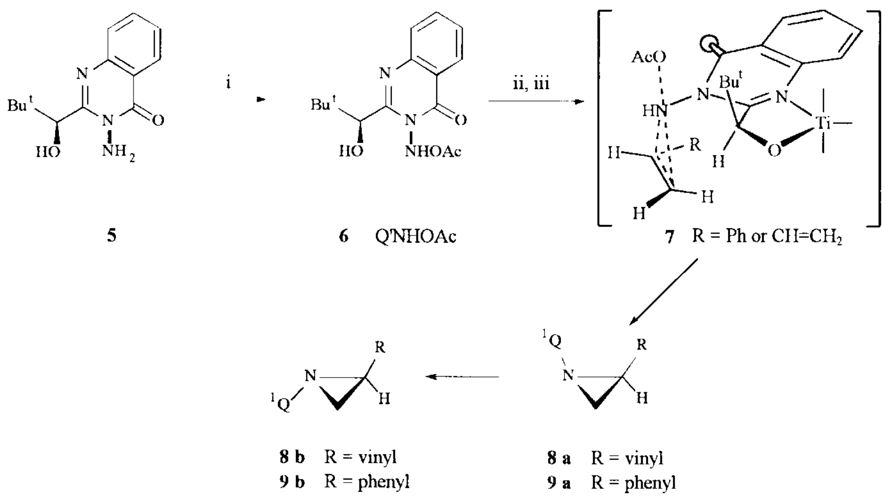
Results

Aziridination of cyclopentadiene

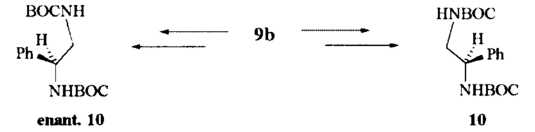
Since the *endo*-overlap in TS$^\#$ **7** requires an s-*cis* conformation for the diene, the enforced s-*cis* diene conformation present in cyclic dienes should make them reactive towards aziridination with QNHOAc. Reactions of cyclopentadiene with three QNHOAc compounds were first examined. With Q^{2}NHOAc **11**, aziridine **12** (42%) was obtained as a crystalline solid: the presence of hexamethyldisilazane (HMDS) in this reaction scavenges acetic acid and raises the yield.[7] Similarly, the use of Q^{3}NHOAc **13** yielded the corresponding aziridine **14** (55%) (Scheme 5): the greater stability of Q^{3}NHOAc **13** often leads to superior yields of aziridination products.[8]

Reaction of cyclopentadiene with Q^{1}NHOAc **6** in the presence of TTB and crystallisation of the crude product from diethyl ether gave aziridine **16a** (25%) (Scheme 6). Although the yield of aziridine **16a** is low, it is isolable without the need for chromatography because it constitutes the major part of the recovered product: the fate of the other Q^{1}NHOAc **6**-derived product(s) is unknown. An X-ray crystal structure determination of **16a**[9] showed that the relative configuration was in agreement with the TS$^\#$ model **15** (*cf.* **7** for butadiene). Unexpectedly, this crystal structure also showed that the quinazolinone and cyclopentene ring residue were *cis* in the aziridine: the Q-substituted nitrogen usually undergoes *N*-inversion

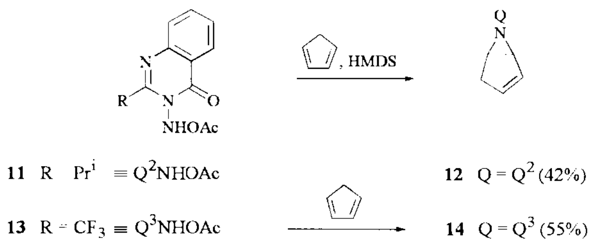
DOI: 10.1039/b102592a



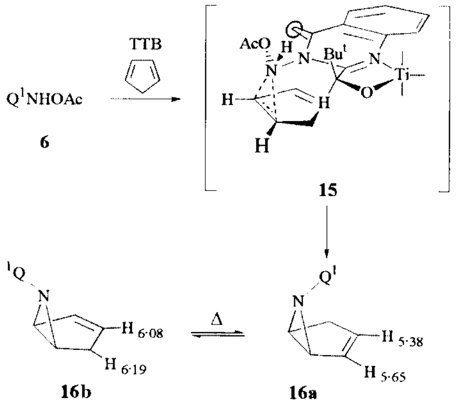
Scheme 3 *Reagents and conditions*: i, LTA, CH_2Cl_2, −20 °C; ii, $Ti(OBu^t)_4$; iii, butadiene or styrene.



Scheme 4



Scheme 5



Scheme 6

at temperatures <−20 °C but in this case the barrier is raised sufficiently for the first-formed *N*-invertomer **16a** to be isolated.[6]

When aziridine **16a** was dissolved in deuteriochloroform and warmed in an NMR tube for 30 min at 60 °C, signals from the *exo*-*N*-invertomer **16b** appeared in the NMR spectrum and a 1 : 1 equilibrium ratio of *N*-invertomers was established which was unchanged on further heating. The *endo*⟶*exo* inversion of Q^1 is accompanied by a downfield shift for the olefinic protons (see Scheme 6).

Aziridination of cyclopentadiene with Q^{1}NHOAc **6** in the absence of TTB gave an unseparated mixture of products whose NMR spectrum suggested the presence of **16a** and its diastereoisomer.

Aziridines **12** and **14** had been previously assumed to be present as their *exo*-*N*-invertomers but in the light of the unexpected stability of *endo*-*N*-invertomer **16a**, samples of each were heated in deuteriochloroform solution for 1 h at 60 °C: no changes in their NMR spectra were observed. A sample of aziridine **12**, moreover, remained unchanged on heating briefly to 200 °C so it can be concluded that *N*-inversion from *endo*⟶*exo* in these aziridines had already occurred in the aziridination. This conclusion was supported by the chemical shifts of the olefinic protons (δ 6.06 and 6.21 for **12**, δ 6.01 and 6.11 for **14**) which resemble closely those in the *exo*-*N*-invertomer **16b** (see Scheme 6).

In aziridine **16a**, therefore, for reasons as yet not clear, the barrier to *N*-inversion, is significantly higher than in **12** and **14** and *endo*- and *exo*-*N*-invertomers are of comparable stability.

The reaction of aziridine **12** with methylcuprate was briefly investigated: using methylmagnesium bromide in the presence of copper(I) bromide, a mixture of products (71%) (Scheme 7) was obtained which could not be separated. Treatment of the mixture with lead tetraacetate (LTA) gave two imines **18** and **19** (68%) in a 1 : 1 ratio whose separation was carried out by Kieselgel chromatography.

The presence of two olefinic protons having very similar multiplicity and coupling constants in imines **18** and **19** suggested that the constitution of each was the same. Their assignments as different *N*-invertomers were supported by the downfield shift of the olefinic proton adjacent to the imine in the NMR spectrum of **18** and the complementary downfield shift of the methylene protons in **19** brought about in each case by the presence of the neighbouring Q group. Support for these structure assignments to imines **18** and **19** came from their interconversion on heating at ~100 °C or even on standing at room temperature over several months.

It appears, therefore, that the mechanism of the cuprate addition is predominantly S_N2' but is probably not very diastereoselective.

Aziridination of cyclohexa-1,3-diene

Reaction of cyclohexa-1,3-diene with Q^{2}NHOAc **11** and with Q^{3}NHOAc **13** in dichloromethane gave the corresponding aziridines **20** (43%) and **21** (59%) (Scheme 8). An X-ray crystal structure determination† of aziridine **21** (Fig. 1) confirmed the expected *exo*-orientation of the Q^3 group. A sample of aziridine **20** was briefly heated to 200 °C and its NMR spectrum was found to be unchanged: the Q^2 group of this aziridine, therefore, can also be assumed to have an *exo*-orientation.

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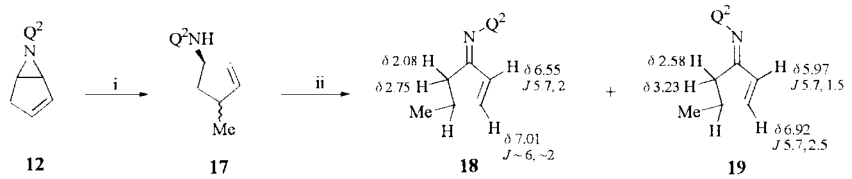
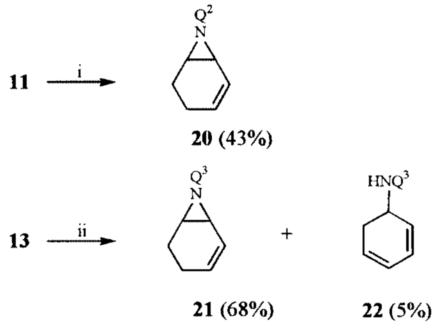
† CCDC reference number 160871. See http://www.rsc.org/suppdata/pl/b1/b102592a/ for crystallographic files in. cif or other electronic format.



Scheme 7 *Reagents and conditions*: i, MeMgBr, CuBr; ii, LTA, −20 °C.



Scheme 8 *Reagents*: i, cyclohexa-1,3-diene, HMDS; ii, cyclohexa-1,3-diene

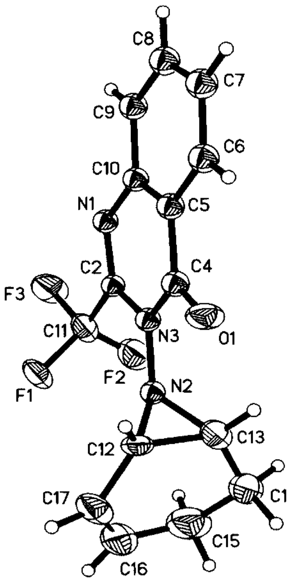


Fig. 1 Molecular structure of **21**, showing the atom label scheme and 30% displacement probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary radius.

A minor product isolated from the aziridination of cyclohexa-1,3-diene with Q^3NHOAc **13** was identified as the dienylamine **22** (5%).

Reaction of cyclohexa-1,3-diene with Q^1NHOAc **6** in the presence of TTB gave a mixture of aziridine **23**, dienylamine **24** and *tert*-butoxyaminoquinazolinone **25**[5] (Scheme 9a).

Aziridine **23** was obtained as a mixture of diastereoisomers in a ratio which varied between 10 : 1 and 4 : 1 in different experiments. The major diastereoisomer was isolated as a colourless solid after crystallisation from ether–light petroleum but with considerable loss in yield. Proof of the stereostructure and the mechanism of formation of dienylamine **24** (and **22**, Scheme 8) will be discussed elsewhere but in the reaction shown in Scheme 9a, dienylamine **24** was not separated from *tert*-butoxyaminoquinazolinone **25**. Neither were the diastereoisomers of aziridine **23** separated by chromatography but their diastereoisomeric relationship was confirmed by the Swern oxidation–sodium borohydride reduction cycle in Scheme 10: a sample diastereomeric ratio (dr) 5 : 1 was converted to a single ketone **26** and then back to a sample of aziridine **23** of dr 3 : 2 showing that the two are epimeric at the aziridine ring chiral centres.

When the reaction of cyclohexa-1,3-diene with Q^1NHOAc **6** was carried out in acetonitrile as solvent, aziridine **23** was obtained in high diastereopurity although in lower yield (38%) (Scheme 9b) together with dienylamine **24** (7%) and two other products. After separation using Kieselgel chromatography, these two products were identified by NMR spectroscopy as *cis*-(Q^1)-amino alcohols **27** and **28**. In the NMR spectrum of each compound there was a coupling of ~3 Hz between the protons on adjacent carbons bearing Q^1NH and OH groups suggesting that these two protons are either both equatorial or equatorial/axial. Since it is likely that the Q^1NH group is equatorial in both compounds, the OH group will be pseudo-axial and hence the two groups are *cis*. Confirmation of these assignments came from conversion of each of these (Q^1)-amino alcohols to the corresponding Q^1-free oxazolidinone enantiomers (see below).

Higher yields of (Q^1)-amino alcohols **27** and **28** were obtained by reaction of aziridine **23** (dr 5 : 1) with toluene-*p*-sulfonic acid in aqueous acetonitrile. After chromatography on deactivated silica, **27** and **28** were isolated in 49 and 13% yields respectively (Scheme 11). An additional product isolated in this reaction was tentatively assigned the cyclic ether structure **29**: this cyclic ether was not formed from a mixture of (Q^1)-amino alcohols **27** and **28** on re-submitting it to the conditions used for the reaction shown in Scheme 11.

Some of the corresponding (Q)-amino alcohol **30** was also obtained, together with aziridine **20** and quinazolin-4(3*H*)-one **31** when cyclohexa-1,3-diene and Q^2NHOAc **11** were reacted together in acetonitrile (Scheme 9c).

Aziridination of cyclohepta-1,3-diene and cycloheptatriene

Reaction of Q^2NHOAc **11** with cyclohepta-1,3-diene gave a crystalline aziridine **32** which was isolated in 36% yield without the need for chromatography. The corresponding reaction of Q^1NHOAc **6**–TTB with cyclohepta-1,3-diene gave a crude product, the major part of which was aziridine **33** (*cf.* aziridination of cyclopentadiene) and which crystallised directly from ethyl acetate–light petroleum in 29% yield.

An X-ray structure determination ‡ of this aziridine (Fig. 2) showed that the relative configuration was the same as that obtained for aziridine **16a** but that the Q^1 group is *exo*.

Aziridine **34** was obtained as a crystalline solid from the reaction of Q^2NHOAc **11** and cycloheptatriene after chromatography: the other isolated product was the quinazolin-4(3*H*)-one **31** (Scheme 12b).

Discussion

Since aziridines **16a** and **33** derived from cyclopentadiene and cyclohepta-1,3-diene respectively both show the same relative and absolute configuration it is likely that the major diastereoisomer from aziridination of cyclohexadiene is also formed with the same sense of diastereoselectivity.

Formation of (Q^1)-amino alcohols **27**, **28** and **30** (Schemes 11 and 9a) by ring-opening of the corresponding aziridines **23** and **21** with retention of configuration is suggestive of the involvement of the Q group in the reaction. Previously, ring-opening

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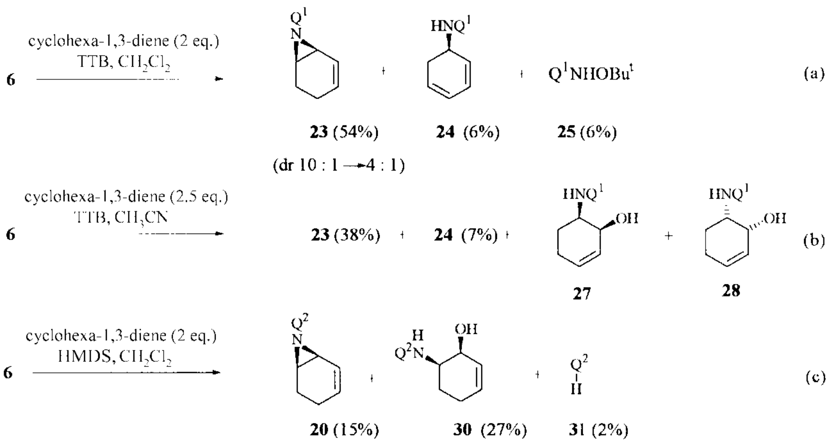
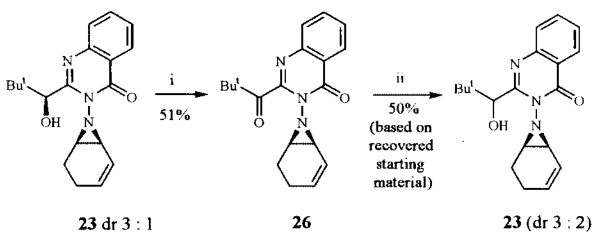
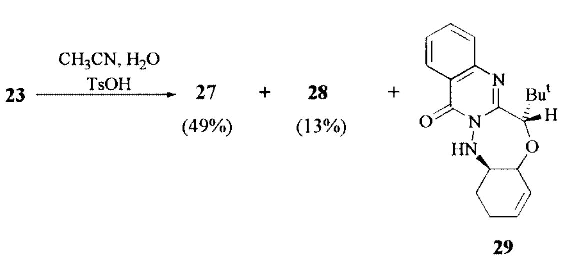
‡ CCDC reference number 160872. See http://www.rsc.org/suppdata/p1/b1/b102592a/ for crystallographic files in .cif or other electronic format.



Scheme 9



Scheme 10 *Reagents*: i, Swern oxidation; ii, NaBH$_4$, EtOH.



Scheme 11

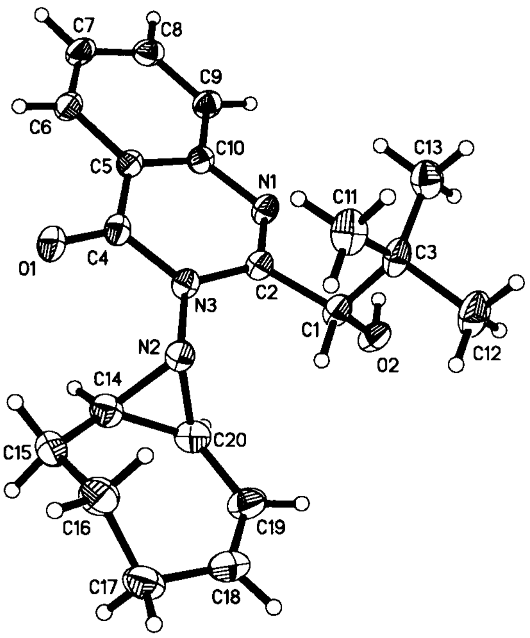
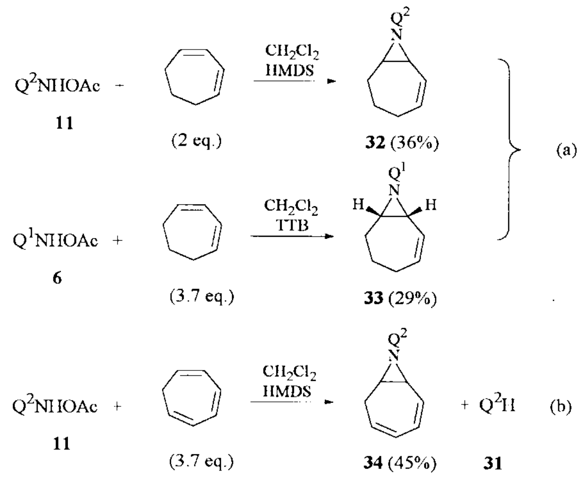


Fig. 2 Molecular structure of **33**, showing the atom label scheme and 30% displacement probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary radius.



Scheme 12

of aziridine **8b** to the corresponding (Q^1)-amino alcohol with aqueous acetic acid was shown to involve participation of the Q^1 carbonyl oxygen.[6]

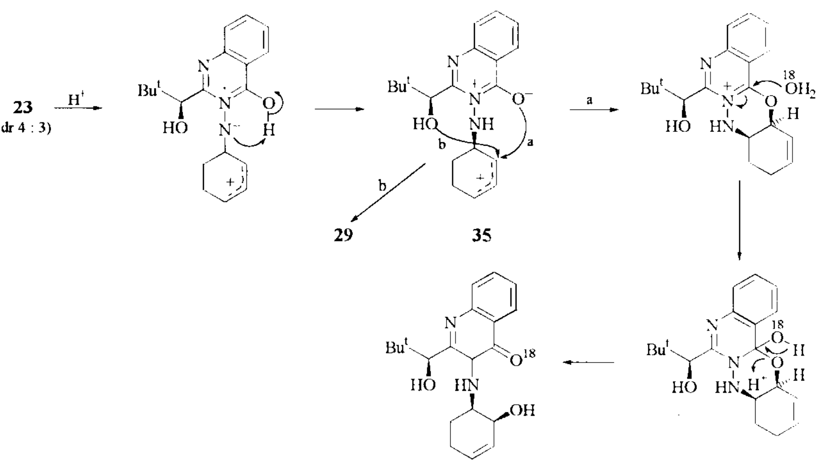
Reaction of a 4 : 1 mixture of aziridine diastereoisomers **23** with toluene-*p*-sulfonic acid in acetonitrile containing ^{18}O-labelled water was interrupted after 45 minutes to allow recovery of unreacted aziridine. Mass spectroscopy showed incorporation as expected of ^{18}O label into the alcohol product but none into the recovered aziridine **23** which supports a mechanism for quinazolinone participation analogous to that proposed previously and illustrated for the reaction of the major aziridine diastereoisomer in Scheme 13.

Recovery of unlabelled aziridine **23** from this reaction serves as a control to eliminate the possibility of exchange of the (Q)C=*O* without its involvement in aziridine ring-opening. Much of the ^{18}O label in the amino alcohol products **27** and **28** was lost on silicon chromatography which supports its presence in the quinazolinone carbonyl group. Scheme 13 also shows a possible competitive reaction (b in **35**) of the allyl cation with the hydroxy group in the Q^1 side-chain giving cyclic ether **29**.

Interestingly, the diastereoisomer ratio (dr) of the recovered aziridine in the experiment above was 10 : 1 and the dr of the alcohol product (**27** : **28**) was ~2 : 1 confirming that the minor aziridine diastereoisomer was ring-opened approximately twice as fast as the major one (and providing an expedient route for purification of the major diastereoisomer **23**). In the light of these results it seems likely that the isolation of only the major aziridine diastereoisomer **23** from aziridination of cyclohexa-1,3-diene with Q^{1}NHOAc **6**–TTB results from faster ring-opening of the minor diastereoisomer by a mechanism resembling that shown in Scheme 13 but mediated by a titanium-containing species instead of by acid.

Conversion of (Q^1)-amino alcohols 27 and 28 into Q^1-free chirons

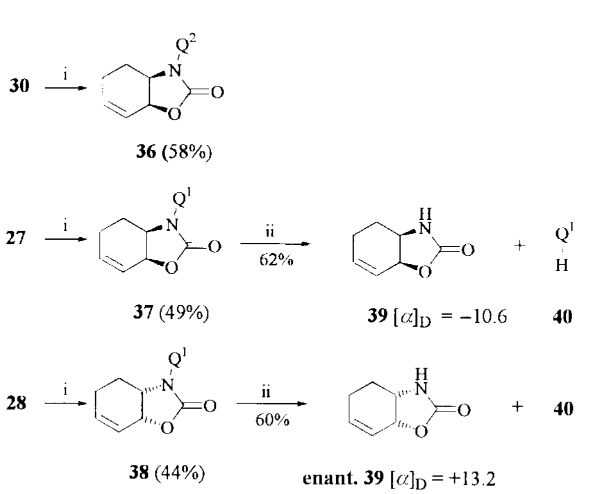
One of the objectives of this work was to use the products from aziridination of dienes with enantiopure QNHOAc reagents



Scheme 13

to prepare Q-free aziridine ring-opened enantiopure products containing two or more chiral centres (chirons).

In a model reaction, Q^3-amino alcohol **30** was heated in THF at reflux with sodium hydride and 1,1′-carbonyldiimidazole for 3 h. Chromatography of the crude product gave oxazolidinone **36** (53%) together with unchanged starting material **30** (35%) (Scheme 14).



Scheme 14 *Reagents and conditions*: i, 1,1′-carbonyldiimidazole, NaH, THF, 3 h; ii, SmI$_2$, Bu^{t}OH, THF.

The similarity in rates of the corresponding reactions of (Q^1)-amino alcohols **27** and **28** with 1,1′-carbonyldiimidazole giving oxazolidinones **37** and **38** respectively supports the previously drawn conclusion that both have *cis*-substituted cyclohexene rings.

Previously we had shown that the presence of a carbonyl group on the exocyclic 3-aminoquinazolinone facilitated reductive cleavage of the N–N bond and allowed aluminium amalgam to be used.[10] However, reduction of oxazolidinones **37** and **38** did not take place with aluminium amalgam but was successful using samarium(II) iodide in the presence of *tert*-butyl alcohol.[10] Q^1-free oxazolidinones **39** and **enant. 39** were separated from quinazolin-4(*3H*)-one Q^{1}H **40** by chromatography and found to have optical rotations which were similar in magnitude but opposite in sign. Assignments of absolute configuration to oxazolidinones **39** and **enant. 39** are based on the assumption that aziridination of cyclohexa-1,3-diene with Q^{1}NHOAc **6** proceeds preferentially with the same diastereosense as in aziridination of butadiene, cyclopentadiene and cyclohepta-1,3-diene.

Summary

Cyclopentadiene and cyclohepta-1,3-diene were mono-aziridinated highly diastereoselectively by Q^{1}NHOAc **6** and TTB in dichloromethane and the crystalline products were isolated without the need for chromatography. Cyclohexa-1,3-diene is aziridinated highly diastereoselectively by Q^{1}NHOAc **6** and TTB in acetonitrile and the product **23** is separated by chromatography from *cis*-Q^1-amino alcohols **27** and **28** formed as by-products.

These enantiopure aziridines could provide a useful source of chirons since Q^{1}NH$_2$ **5**, the precursor of Q^{1}NHOAc **6**, is available from *tert*-leucine in 43% yield (5 steps) without the need for chromatography. Thus the two (Q^1)-amino alcohols **27** and **28** have been converted into enantiomeric Q^1-free oxazolidinones **39** and **enant. 39**.

Experimental

For details of instrumentation and other experimental details see refs. 5 and 6.

General procedure A for aziridination of dienes using Q^{2}NHOAc 11 and Q^{3}NHOAc 13

Dry dichloromethane (1 cm^3 for each 0.1 g QNH$_2$) was added to a round-bottom flask suspended in a dry ice–acetone bath at −12 °C and magnetically stirred. Lead(IV) acetate (LTA; 1.05 mol equiv.) was added to the flask in one portion. When the LTA had dissolved, the temperature of the bath was lowered to −20 °C and the appropriate QNH$_2$ (1.0 mol equiv.) added in small portions over 10–15 min at this bath temperature, stirring throughout. The temperature of the bath was allowed to rise to −10 °C and the solution was filtered into a flask maintained at −10 °C to remove the lead diacetate produced (on a small scale, a Pasteur pipette and a cotton wool plug can be used). To this filtered solution containing the QNHOAc, the diene (1.5–3 mol equiv.) and (with Q^{2}NH$_2$ only) hexamethyldisilazane (3 mol equiv.) were added, the cooling bath removed and the temperature allowed to reach ambient (~15 min) stirring throughout. The reaction mixture was filtered, the filtrate was washed with saturated aqueous sodium hydrogencarbonate solution and water, dried and the solvent evaporated under reduced pressure.

General procedure B for the aziridination of dienes using Q^{1}NHOAc 6 in the presence of titanium(IV) *tert*-butoxide[5]

Procedure A was followed up to and including addition of Q^{1}NH$_2$ **5** and the cold (−10 °C) solution filtered through a cotton wool plug into a stirred solution of titanium(IV) *tert*-butoxide (2.1 equiv.) held at −20 °C. After stirring at this temperature for 2 min the alkene (2 equiv.) was added and the temperature of the reaction mixture allowed to rise to ambient by removal of the cooling bath. Saturated sodium hydrogencarbonate solution was added to the vigorously stirred reaction mixture and a gelatinous precipitate formed immediately. The solution was filtered through Celite and the organic layer of the filtrate was separated, washed with brine, dried, and the solvent evaporated under reduced pressure to give the crude product.

Aziridination of cyclopentadiene using Q^{2}NHOAc 11

General aziridination procedure **A** was followed using 3-amino-2-isopropylquinazolin-4(3*H*)-one[11] (300 mg, 1.47 mmol), LTA (687 mg, 1.55 mmol), HMDS (474 mg, 2.94 mmol) and cyclopentadiene (194 mg/0.24 cm^3, 2.94 mmol) in dichloromethane (6 cm^3). Crystallisation of the crude product (457 mg) from ethyl acetate–light petroleum gave *aziridine* **12** (159 mg, 42%) as a colourless solid, mp 126–128 °C (from ethyl acetate–light petroleum) (Found: C, 71.5; H, 6.4; N, 15.7%. $C_{16}H_{17}ON_3$ requires C, 71.8; H, 6.4; N, 15.7%); ν_{max}/cm^{-1} 1670s, 1470m and 1380s; δ_H 1.40 (3H, d, *J* 6.6, C*H*$_3$CHCH$_3$), 1.42 (3H, d, *J* 6.6, CH$_3$CHC*H*$_3$), 2.76 (1H, dddd, *J* 18.9, 5.0, ~2 and ~2, C*H*H), 2.95 (1H, ddd, *J* 18.9, ~2 and ~2, CH*H*), 3.60 (1H, br d, *J* ~5 and ~5, azir. NC*H*CH$_2$), 3.67 [1H, heptet, *J* 6.6, C*H*(CH$_3$)$_2$], 3.79 (1H, br d, *J* ~5, azir. NC*H*C=C), 6.3–6.9 (1H, struct. m, C*H*=CH), 6.21 (1H, dddd, *J* 5.6, ~2, ~2, ~2, CH=C*H*), 7.40 [1H, ddd, *J* 8.2, 6.9, 1.5, H-6(Q)], 7.59–7.72 [2H, struct. m, H-7, H-8 (Q)] and 8.19 [1H, dd, *J* 8.2, 1.0, H-5(Q)]; δ_C 21.6, 32.7 (2 × CH$_3$), 36.7 (CH$_2$), 49.5 [*C*H(CH$_3$)$_2$], 52.5, 58.1 (2 × C–N), 121.8 [*C*CO(Q)], 126.4, 126.5, 127.3, 128.4, 133.9, 138.5 [4 × CH(Q) and H*C*=*C*H], 146.6 [*C*N=C(Q)] and 160.4, 161.8 [CN(Q), CO(Q)]; *m*/*z*(%) 267 (M$^+$,10), 189 (12), 188 (43), 187 (27) and 173 (100).

Aziridination of cyclopentadiene using Q^3 NHOAc 13

3-Amino-2-trifluoromethylquinazolin-4(3*H*)-one (Q^{3}NH$_2$) was prepared by the published route[7] except that the crude 2-trifluoromethyl-3,1-benzoxazin-4-one was treated with hydrazine in ethanol directly after removal of trifluoroacetic anhydride. Following general procedure **A**, the foregoing Q^{3}NH$_2$ (300 mg, 1.31 mmol), LTA (609 mg, 1.38 mmol) and cyclopentadiene (173 mg/0.22 cm^3, 2.62 mmol) were reacted in dichloromethane (6 cm^3). Crystallisation of the crude product (309 mg) from ethyl acetate–light petroleum gave *aziridine* **14** (212 mg, 55%) as a colourless solid, mp 125–127 °C (from ethyl acetate–light petroleum) (Found: M$^+$ 293.0775. $C_{14}H_{10}ON_3F_3$ requires *M* 293.0775); ν_{max}/cm^{-1} 1665s, 1470m and 1390s; δ_H 2.70 (1H, dddd, *J* 18.8, 5.0, ~2, ~2, C*H*H), 2.85 (1H, ddd, *J* 18.8, ~2, ~2, CH*H*), 4.04 (1H, br dd, *J* ~5, ~5, azir. NC*H*CH$_2$), 4.28 (1H, br d, *J* ~5, azir. NC*H*C=C), 6.01 (1H, struct. m, C*H*=CH), 6.11 (1H, struct. m, CH=C*H*), 7.59 [1H, ddd, *J* 8.2, ~4, ~4, H-6(Q)], 7.75–7.82 [2H, m, H-7, H-8(Q)] and 8.24 [1H, br d, *J* 8.2, H-5(Q)]; δ_C 38.6 (CH$_2$), 49.1, 55.0 (2 × C–N), 123.3 [*C*CO(Q)], 127.0, 128.8, 129.0, 129.5, 134.9, 138.4 [4 × CH(Q) and H*C*=*C*H], 144.3 [*C*N=C(Q)] and 160.5, 170.2 [CN(Q), CO(Q)]; *m*/*z*(%) 293 (M$^+$, 7), 215 (100), 214 (70) and 213 (38).

Aziridination of cyclopentadiene using Q^{1}NHOAc 6 and TTB

General aziridination procedure **B** was followed in this reaction using Q^{1}NH$_2$ **5** (200 mg, 0.80 mmol), LTA (376 mg, 8.50 mmol), TTB (576 mg, 1.71 mmol) and cyclopentadiene (105 mg/131 cm^3, 1.59 mmol) in dichloromethane (5 cm^3). Crystallisation of the crude product from diethyl ether gave *endo-aziridine* **16a** (60 mg, 25%) as a colourless solid, mp 126–128 °C (from diethyl ether–light petroleum). $[a]_D = +1.3$ ($c = 1.1$, EtOH) (Found: C, 69.1; H, 6.8; N, 13.4%. $C_{18}H_{21}O_2N_3$ requires C, 69.4; H, 6.8; N, 13.4%); ν_{max}/cm^{-1} 1675s, 1610m and 1590s; δ_H 1.00 [9H, s, C(CH$_3$)$_3$], 2.43 (1H, ddd, *J* 20.1, ~5, ~2, C*H*H), 2.63 (1H, dddd, *J* 20.1, 5.5, ~2, ~2, CH*H*), 3.58 (1H, br dd, *J* ~5, ~5, azir. NC*H*CH$_2$), 3.85 (1H, d, *J* 10.6, CHO*H*), 4.19–4.22 (1H, m, azir. NC*H*C=C), 4.75 (1H, d, *J* 10.6, C*H*OH), 5.35–5.41 (1H, m, C*H*=CH), 5.65 (1H, dddd, *J* 5.7, ~2, ~2, ~2, CH=C*H*), 7.42 [1H, ddd, *J* 8.2, 6.9, 1.0, H-6(Q)], 7.62 [1H, dd, *J* 8.2, 1.0, H-8(Q)], 7.70 [1H, ddd, *J* 8.2, 6.9, 1.0, H-7(Q)] and 8.17 [1H, dd, *J* 8.2, 1.0, H-5(Q)]; δ_C 26.3 [C(*C*H$_3$)$_3$], 38.6 (C), 39.4 (CH$_2$), 50.6, 57.0 (2 × C-N), 75.3 (C-OH), 121.9 [*C*CO(Q)], 126.2, 126.6, 126.8, 127.2, 132.8, 134.0 [4 × CH(Q) and H*C*=*C*H], 145.1 [*C*N=C(Q)] and 156.9, 158.2 [CN(Q) and CO(Q)]; *m*/*z*(%) 311 (M$^+$, 4) and 176 (100).

Thermal equilibration of *endo*-aziridine 16a and *exo*-aziridine 16b

endo-Aziridine **16a** (50 mg, 0.16 mmol) was heated in CDCl$_3$ at 60 °C for 30 min. On cooling, the NMR spectrum showed, in addition to the signals above belonging to *endo*-aziridine **16a**, those assignable to *exo*-aziridine **16b** at δ_H 1.02 [9H, s, C(CH$_3$)$_3$], 2.74 (1H, dddd, *J* 18.8, ~5, ~2, ~2, C*H*H), 2.99 (1H, ddd, *J* 18.8, ~5, ~2, C*H*H), 3.63 (1H, br d, *J* ~6, azir. NC*H*C=C), 3.84 (1H, d, *J* 10.4, CHO*H*), 3.99 (1H, br dd, *J* ~5, ~5, azir. NC*H*CH$_2$), 5.01 (1H, d, *J* 10.4, C*H*OH), 6.07 (1H, m, C*H*=CH), 6.14 (1H, struct. m, CH=C*H*), 8.21 [1H, dd, *J* 8.2, 1.0, H-5(Q)]; δ_C 25.9 [C(CH$_3$)$_3$], 32.5 (CH$_2$), 38.1 (C), 51.2, 56.6 (2 × C–N), 75.0 (C–OH), 121.5 [*C*CO(Q)], 125.8, 126.4, 127.0 [3 × CH(Q)], 129.0, 133.6, 139.2 [H*C*=*C*H and CH(Q)], 144.8 [*C*N=C(Q)] and 157.9, 159.6 [CN(Q), CO(Q)].

Reaction of aziridine 12 with cuprate

A flame dried 2-necked flask equipped with a septum cap and 3-way tap was flushed with nitrogen, degassed, flushed with argon, degassed and filled with argon. Using syringes, a suspension of copper(I) bromide–dimethyl sulfide (58 mg, 0.28 mmol) (prepared by the literature procedure[12]) and dissolved in THF (1 cm^3) was added followed by methylmagnesium bromide (101 mg/0.1 cm^3, 0.84 mmol) dissolved in THF (1 cm^3). Aziridine **16a** (75 mg, 0.28 mmol), dissolved in THF (1 cm^3), was then added dropwise *via* a syringe to the solution which was stirred at ambient temperature for 1 h. After addition of ethyl acetate (5 cm^3) the solution was washed with saturated aqueous sodium hydrogencarbonate (5 cm^3) and the solvent separated, dried and evaporated. Column chromatography (3 : 1 light petroleum–ethyl acetate) of the crude product (80 mg) gave a mixture of (Q^2)amines **17** (58 mg, 71%) as a yellow oil, R_f 0.28.

LTA oxidation of (Q^2)amines 17

The above mixture of amines **17** (58 mg, 0.20 mmol) was dissolved in dichloromethane (1 cm^3) at −20 °C and HMDS (72 mg, 0.45 mmol) was added. LTA (95 mg, 0.21 mmol) was added in small portions over 10 min and the solution allowed to warm to ambient temperature. Dichloromethane (10 cm^3) was added and the solution washed with saturated aqueous sodium hydrogencarbonate (5 cm^3), the organic layer separated, dried and evaporated to give the crude product as a yellow oil. Column chromatography (2 : 1 light petroleum–ethyl acetate) gave *N(Q^2)-imine* **18** (18 mg, 33%) as a colourless oil, R_f 0.43 (Found: M$^+$ 281.1529. $C_{17}H_{19}ON_3$ requires *M* 281.1528); ν_{max}/cm^{-1} 1780 m, 1675s, 1620s and 1595 m; δ_H 1.13 (3H, d, *J* 6.9, CHC*H*$_3$), 1.29 (3H, d, *J* ~7, CHC*H*$_3$), 1.30 (3H, d, *J* ~7, CHC*H*$_3$), 2.08 (1H, dd, *J* 18.6, ~2, C*H*H), 2.75 (1H, dd, *J* 18.6, ~6, C*H*H), 3.02 (1H, struct. m, C*H*Me), 3.31 [1H, heptet, *J* 6.9, C*H*(CH$_3$)$_2$], 6.55 (1H, dd, *J* 5.7, 2.2, C*H*=CHC=N), 7.01 (1H, br dd, *J* ~6, ~2, N=CCH=C*H*), 7.43 [1H, ddd, *J* ~8, ~6, ~3, H-6(Q)], 7.69–7.73 [2H, m, H-7 and H-8(Q)] and 8.29 [1H, dd, *J* 8.2, 1.0, H-5(Q)]; *m*/*z* (%) 281 (M$^+$, 78), 266 (100), 187 (81) and 173 (73).

Further elution gave *N(Q^2)-imine* **19** (19 mg, 35%) as a colourless oil, R_f 0.36 (Found: M$^+$ 281.1529. $C_{17}H_{19}ON_3$ requires *M* 281.1528); ν_{max}/cm^{-1} 1780 m, 1675s, 1620s and 1595 m; δ_H 1.24 (3H, d, *J* 6.9, CHC*H*$_3$), 1.28 (6H, d, *J* ~7, 2 × CHC*H*$_3$), 2.55 (1H, dd, *J* 18.1, ~2, C*H*H), 3.14 (1H, struct. m, C*H*Me), 3.23 (1H, dd, *J* 18.1, 6.9, C*H*H), 3.36 [1H, heptet, *J* 6.6, C*H*(CH$_3$)$_2$], 5.97 (1H, dd, *J* 5.7, 1.5, C*H*=CHC=N), 6.92 (1H, dd, *J* 5.7, 2.5, N=CCH=C*H*), 7.42 [1H, ddd, *J* 8.2, 6.9, 1.2, H-6(Q)], 7.69–7.73 [2H, m, H-7 and H-8(Q)] and 8.26 [1H, d, *J* 8.2, H-5(Q)]; *m*/*z*(%) 281 (M^+, 71), 266 (100), 188 (53), 187 (96) and 173 (91).

A sample of imine **18** which had been set aside for 18 months was found to have partially interconverted with imine **19** (ratio ~2 : 1 respectively).

Aziridination of cyclohexa-1,3-diene with Q^2NHOAc 11

General aziridination procedure **A** was followed in this reaction using 3-amino-2-isopropylquinazolin-4(3*H*)-one[11] (600 mg, 2.96 mmol), LTA (1.38 g, 3.11 mmol), HMDS (1.19 g, 7.40 mmol) and cyclohexa-1,3-diene (470 mg/0.55 cm^3, 5.92 mmol) in dichloromethane (12 cm^3). Column chromatography of the crude product (0.68 g) using 2 : 1 light petroleum–ethyl acetate gave *aziridine* **20** (0.54 g, 60%) as a colourless solid, R_f 0.41, mp 93–95 °C (from light petroleum–ethyl acetate) (Found: MH^+ 282.1606. $C_{17}H_{20}ON_3$ requires MH^+ 282.1607); ν_{max}/cm^{-1} 1660s and 1570s; δ_H 1.32 (3H, d, *J* 6.6, C*H*$_3$CHCH$_3$), 1.35 (3H, d, *J* 6.6, C*H*$_3$CHC*H*$_3$), 1.69 (1H, struct. m, CH$_2$C*H*H), 2.13 (1H, ddd, *J* ~18, ~6, ~6, C*H*HCH$_2$), 2.27 (1H, struct. m, incl. *J* 18.0, CH*H*CH$_2$), 2.61 (1H, dddd, *J* ~15, ~7, ~2, ~2, CH$_2$CH*H*), 2.94 (1H, dd, *J* 7.9, 4.7, azir. NCHCH$_2$), 3.36 (1H, dd, *J* 7.9, 2, azir. NC*H*C=C), 3.64 [1H, heptet, *J* 6.6, C*H*(CH$_3$)$_2$], 6.03 (1H, ddd, *J* 8.7, ~6, ~2, C*H*=CH), 6.23 (1H, ddd, *J* 8.7, ~6, ~4, CH=C*H*), 7.42 [1H, ddd, *J* 8.1, 6.3, 1.2, H-6(Q)], 7.60–7.70 [2H, m, H-7 and H-8(Q)] and 8.20 [1H, dd, *J* 8.1, 1.2, H-5(Q)]; δ_C 20.4 (CH$_2$), 22.7 (CH$_3$), 23.1 (CH$_2$), 23.4 (CH$_3$), 33.3 [*C*H(CH$_3$)$_2$], 45.8, 50.8 (2 × C–N), 123.3, 123.6 [H*C*=*C*H, *C*CO(Q)], 128.3, 129.2, 135.5, 135.7 [4 × *C*H(Q)], 148.4 [*C*N=C(Q)] and 162.4, 163.7 [CN(Q), CO(Q)]; *m*/*z*(%) 282 (MH^+, 100) and 189 (45).

Aziridination of cyclohexa-1,3-diene with Q^3NHOAc 13

General aziridination procedure **A** was followed using 3-amino-2-trifluoromethylquinazolin-4(3*H*)-one (see above; 200 mg, 0.87 mmol), LTA (406 mg, 0.92 mmol) and cyclohexa-1,3-diene (140 mg/0.16 cm^3, 1.75 mmol) in dichloromethane (4 cm^3). Crystallisation of the crude product (246 mg) from ethyl acetate–light petroleum gave *aziridine* **21** (170 mg) as a white solid, mp 103–105 °C (Found: C, 58.6; H, 3.85; N, 13.7%. $C_{15}H_{13}ON_3F_3$ requires C, 58.6; H, 3.9; N, 13.7%); ν_{max}/cm^{-1} 1690s, 1610s, 1470m and 1380s; δ_H 1.43 (1H, dddd, *J* 14.0, 10.0, 6.7, ~2, CH$_2$C*H*H), 1.91 (1H, ddd, *J* 17.5, ~7, ~7, C*H*HCH$_2$), 2.05 (1H, struct. m, incl. *J* 17.5, CH*H*CH$_2$), 2.23 (1H, dddd, *J* 14.0, 7.8, ~2, ~2, CH$_2$CH*H*), 3.59 (1H, dd, *J* 7.5, 4.8, azir. NC*H*CH$_2$), 3.82 (1H, d, *J* 7.5, azir. NC*H*C=C), 5.82 (1H, m, C*H*=CH), 5.97 (1H, ddd, *J* 9.5, ~5, ~3, CH=C*H*), 7.41 [1H, ddd, *J* 8.2, 4.9, 3.2, H-6(Q)], 7.60–7.69 [2H, m, H-7 and H-8(Q)] and 8.04 [1H, dd, *J* 8.0, 1.0, H-5(Q)]; δ_C 18.6, 21.2 (2 × CH$_2$), 38.5, 44.1 (2 × C–N), 122.1, 123.3 [*C*CO(Q), H*C*=CH], 127.2, 128.6, 129.3 [3 × CH(Q)], 133.1, 134.9 [CH(Q), HC=*C*H], 144.3 [*C*N=C(Q)], 160.9, 162.3 [CN(Q), CO(Q)]–(*C*F$_3$ not visible); *m*/*z*(%) 308 (MH^+, 100), 230 (24), 215 (46).

Kieselgel chromatography (2 : 1 light petroleum–ethyl acetate) of the residue after evaporation of the filtrate above gave more aziridine **21** (13 mg, total 68%), R_f 0.41.

A crystal suitable for X-ray crystallography was prepared by crystallisation from light petroleum.

Further elution gave the *dienylamine* **22** (13 mg, 5%) as a clear colourless oil, R_f 0.33 (Found: MH^+ 308.1011. $C_{15}H_{13}ON_3F_3$ requires MH^+ 308.1011); ν_{max}/cm^{-1} 1695m and 1610m; δ_H 2.31 (1H, dddd, *J* ~18, ~8, ~4, ~2, C*H*H), 2.45 (1H, dddd, *J* 18.0, 5.0, 5.0, ~1.5, CH*H*), 3.93 (1H, m, incl. *J* ~11, C*H*NH), 5.43 (1H, d, *J* 11, NH), 5.83 (1H, dd, *J* 9.6, 5.1, C*H*=CH), 5.90 (1H, dddd, *J* 10.5, 5.9, ~4, ~2, CH=C*H*), 6.03 (1H, m, C*H*=CH), 6.13 (1H, dddd, *J* 9.6, 5.0, ~1, ~1, CH=C*H*), 7.64 [1H, ddd, *J* 8.0, ~4, ~4, H-6(Q)], 7.81–7.86 [2H, m, H-7 and H-8(Q)] and 8.31 [1H, dd, *J* 8.2, 1.0, H-5(Q)]; δ_C(75 MHz) 28.3 (CH$_2$), 54.2 (CNH), 122.5 [*C*CO(Q)], 123.8, 124.0, 126.1, 127.3, 127.6, 129.2, 129.6, 135.5 [4 × CH(Q) and 2 × H*C*=*C*H], 145.3 [*C*N=C(Q)] and 162.4, 168.3 [CN(Q), CO(Q)]; *m*/*z*(%) 308 (MH^+, 44), 307 (M^+, 42), 230 (100) and 229 (50).

Aziridination of cyclohexa-1,3-diene with Q^1NHOAc 6–TTB

General aziridination procedure **B** was followed using Q^1NH_2 **5** (500 mg, 2.01 mmol), LTA (942 mg, 2.12 mmol), TTB (1.42 g, 4.20 mmol) and cyclohexa-1,3-diene (320 mg/0.38 cm^3, 4.00 mmol) in dichloromethane (11 cm^3). After work up, column chromatography (8 : 1 light petroleum–ethyl acetate) gave a mixture of *dienylamine* **24** (37 mg, 6%) and *tert*-butoxyaminoquinazolinone **25** (26 mg, 6%) as a colourless oil, R_f 0.17. For dienylamine **24**: $[\alpha]_D$ = +12.9 (*c* = 1.0, EtOH) (Found: M^+ 325.1791. $C_{19}H_{23}O_2N_3$ requires *M* 325.1790); ν_{max}/cm^{-1} 3500m, 1675s, 1595s and 1470s; δ_H 0.96 [9H, s, (CH$_3$)$_3$], 2.37 (2H, m, CH$_2$), 3.61 (1H, d, *J* 10.4, CHO*H*), 3.96 (1H, ddd, *J* ~12, ~6, ~6, C*H*NH), 5.13 (1H, d, *J* 10.4, C*H*OH), 5.37 (1H, d, *J* 5.9, NH), 5.58 (1H, br dd, *J* ~9, ~5, C*H*=CH), 5.92 (1H, m, CH=C*H*), 6.05 (1H, m, C*H*=CH), 6.15 (1H, m, CH=C*H*), 7.48 [1H, ddd, *J* 8.2, 6.9, 1.0, H-6(Q)], 7.69 [1H, d, *J* 8.2, H-8(Q)], 7.78 [1H, ddd, *J* 8.2, 6.9, 1.0, H-7(Q)] and 8.23 [1H, dd, *J* 8.2, 1.0, H-5(Q)]; δ_C(75 MHz) 26.3 [(*C*H$_3$)$_3$], 28.3 (CH$_2$), 38.3 [*C*(CH$_3$)$_3$], 52.0 (C-N), 75.2 (COH), 120.3 [*C*CO(Q)], 122.9, 123.8, 126.3, 127.1, 127.2, 127.7, 128.2, 134.9 [2 × H*C*=*C*H and 4 × CH(Q)], 146.9 [*C*N=C(Q)] and 160.6, 161.8 [CN(Q), CO(Q)]; *m*/*z*(%) 326 (MH^+, 52), 248 (48), 233 (100) and 215 (36). 3-*tert*-Butoxyaminoquinazolinone **25** was identified by comparison of signals at δ 0.97 and 1.36 (lit.[5] 0.91 and 1.27) in its ^{1}H NMR spectrum.

Further elution gave *aziridine* **23** (291 mg, 54%) as a colourless gum, R_f 0.11, which crystallised from diethyl ether–light petroleum, mp 106–107 °C. $[\alpha]_D$ = +16.9 (*c* = 2.5, EtOH) (Found: M^+ 325.1790. $C_{19}H_{23}O_2N_3$ requires *M* 325.1790); ν_{max}/cm^{-1} 3480m, 1660s and 1580s; δ_H 1.02 [9H, s, C(CH$_3$)$_3$], 1.65 (1H, dddd, *J* 13.0, 12.5, 7.5, ~3, C*H*HCH$_2$), 2.15–2.20 (2H, m, C*H*$_2$), 2.66 (1H, dddd, *J* ~13, ~8, ~2, ~2, CH*H*CH$_2$), 2.91 (1H, ddd, *J* 7.7, 4.7, 1.0, azir. NC*H*CH$_2$), 3.57 (1H, br d, *J* 7.7, azir. NCHC=C), 3.82 (1H, d, *J* 10.4, CHO*H*), 5.04 (1H, d, *J* 10.4, C*H*OH), 6.03 (1H, m, C*H*=CH), 6.22 (1H, m, CH=C*H*), 7.44 [1H, ddd, *J* 8.2, 6.9, 1.0, H-6(Q)], 7.64 [1H, d, *J* 8.0, H-8(Q)], 7.70 [1H, ddd, *J* 8.0, 6.9, 1.2, H-7(Q)] and 8.21 [1H, dd, *J* 8.2, 1.2, H-5(Q)]; δ_C 18.4, 21.6 (2 × CH$_2$), 26.3 [C(*C*H$_3$)$_3$], 38.5 [*C*(CH$_3$)$_3$], 45.5, 48.7 (2 × C-N), 75.1 (COH), 120.7, 121.8 [*C*CO(Q), HC=*C*H], 126.3, 126.7, 127.0, 127.4, 134.1 [4 × CH(Q), H*C*=CH], 145.0 [*C*N=C(Q)] and 158.0, 159.9 [CN(Q), CO(Q)]; *m*/*z*(%) 325 (M^+, 48), 268 (62), 240 (100), 231 (94) and 215 (80). The NMR spectrum of aziridine **23** before crystallisation showed the presence of another diastereoisomer with (observable signals)—δ_H 0.99 [9H, s, C(CH$_3$)$_3$], 2.47 (1H, struct. m, C*H*H), 3.85 (1H, d, *J* 10.3, CHO*H*) and 5.02 (1H, d, *J* 10.3, C*H*OH). The ratio of aziridine diastereoisomers ranged from 10 : 1–4 : 1 in different experiments from comparison of signals at δ 2.66 and 2.47 in the ^{1}H NMR spectrum of the crude reaction product.

Swern oxidation of aziridine 23

DMSO (73 mg/0.07 cm^3, 0.93 mmol) was added to dichloromethane (1 cm^3) pre-cooled to −78 °C followed by dropwise addition of oxalyl chloride (60 mg, 0.46 mmol). After stirring for 10 min, aziridine **23** (dr 5 : 1) (100 mg, 0.31 mmol) was added to a solution of dichloromethane (1 cm^3) and the mixture stirred at −78 °C for 2 h. Triethylamine (219 mg, 2.17 mmol) was added and the solution warmed to ambient temperature. After addition of saturated sodium hydrogencarbonate solution (10 cm^3) and extraction with dichloromethane (15 cm^3), drying of the organic layer and evaporation gave the crude product as a yellow oil. Column chromatography (3 : 1 light petroleum–ethyl acetate) gave *ketone* **26** (51 mg, 51%) as a colourless oil, R_f 0.50 (Found: MH^+ 324.1712. $C_{19}H_{22}O_2N_3$ requires MH^+ 324.1712); δ_H 1.32 [9H, s, (CH$_3$)$_3$], 1.46–1.61

(1H), 2.00–2.08 (2H) and 2.30–2.39 (1H) (3 × m, C*H*$_2$C*H*$_2$), 3.69 (1H, ddd, *J* 7.8, 4.8, 1.5, azir. C*H*CH$_2$), 3.97 (1H, ddd, *J* 7.8, ~2, ~2, azir. C*H*C=C), 5.88 (1H, m, C*H*=CH), 6.06 (1H, m, CH=C*H*), 7.48 [1H, ddd, *J* 8.0, 6.6, 1.1, H-6(Q)], 7.66 [1H, dd, *J* 8.0, 1.1, H-8(Q)], 7.75 [1H, ddd, *J* 8.0, 6.6, 1.3, H-7(Q)] and 8.21 [1H, dd, *J* 8.0, 1.3, H-5(Q)]; δ_C 18.2 (CH$_3$)$_3$, 21.4, 27.1 (2 × CH$_2$), 40.4, 44.9, 45.0 [2 × C-N, *C*(CH$_3$)$_3$], 122.5, 122.8 [H*C*=CH, *C*CO(Q)], 126.7, 127.6, 128.0, 132.9, 134.5 [4 × CH(Q), HC=*C*H], 146.2 [*C*N=C(Q)], 153.2, 160.3 [CN(Q), CO(Q)] and 204.9 (C=O); *m*/*z*(%) 324 (MH$^+$, 31), 246 (22), 231 (100) and 215 (44).

Further elution gave unreacted aziridine **23** (19 mg, 19% recovered), R_f 0.23.

Sodium borohydride reduction of ketone 26

Ketone **26** (50 mg, 0.16 mmol) was stirred in ethanol (5 cm^3) with sodium borohydride (3 mg, 0.05 mmol) at ambient temperature for 4 h. Addition of saturated sodium hydrogencarbonate solution (10 cm^3) and extraction with ethyl acetate (10 cm^3), drying and then evaporation of the organic layer gave the crude product as a colourless oil. Column chromatography (3 : 1 light petroleum–ethyl acetate) gave ketone **26** (14 mg, 28% recovered) as a colourless oil, R_f 0.51.

Further elution gave aziridine **23** (18 mg, 36%) as a colourless oil, R_f 0.30, in which the two aziridine diastereoisomers **23** were now present in a 3 : 2 ratio from comparison of signals at δ 3.57 and 3.85 in its ^{1}H NMR spectrum.

Aziridination of cyclohepta-1,3-diene with Q^{2}NHOAc 11

The reaction was carried out following general aziridination procedure **A** using 3-amino-2-isopropylquinazolin-4(3*H*)-one[11] (300 mg, 1.48 mmol), LTA (689 mg, 1.55 mmol), HMDS (597 mg, 3.70 mmol) and cyclohepta-1,3-diene (272 mg/0.30 cm^3, 2.96 mmol) in dichloromethane (6 cm^3). After work up the crude product was obtained as an off-white solid which was crystallised from ethyl acetate–light petroleum giving *aziridine* **32** (135 mg, 31%) as a white crystalline solid, mp 230–231 °C (Found: C, 72.9; H, 7.0; N, 14.2%. C$_{18}$H$_{22}$ON$_3$ requires C, 73.1; H, 7.1; N, 14.2%); ν_{max}/cm^{-1} 1660s and 1585m; δ_H 1.40 (3H, d, *J* 6.4, C*H*$_3$CHCH$_3$), 1.42 (3H, d, *J* 6.4, CH$_3$CHC*H*$_3$), 1.63–1.84 (2H, struct. m, 2 × C*H*), 2.04–2.19 (1H, m, 2 × C*H*), 2.27–2.42 (1H, m, C*H*), 2.51–2.64 (1H, m, C*H*), 2.94 (1H, br dd, *J* 8.0, ~5, azir. C*H*), 3.18 (1H, ddd, *J* 8.0, ~4, ~4, azir. C*H*), 3.65 [1H, heptet, *J* 6.4, C*H*(CH$_3$)$_2$], 5.95 (1H, ddd, *J* 11.4, 6.6, 3.2, C*H*=CH), 6.13 (1H, br ddd, *J* 11.4, ~5, ~2.5, CH=C*H*), 7.39 [1H, ddd, *J* 8.2, 6.8, 1.0, H-6(Q)], 7.62 [1H, dd, *J* 8.2, 1.0, H-8(Q)], 7.67 [1H, ddd, *J* 8.2, 6.8, 1.2, H-7(Q)] and 8.18 [1H, dd, *J* 8.2, 1.2, H-5(Q)]; δ_C 21.4, 21.5 [CH(*C*H$_3$)$_2$], 23.7, 28.9 (2 × CH$_2$), 31.1 [*C*H(CH$_3$)$_2$], 31.9 (CH$_2$), 50.6, 54.7 (2 × C-N), 121.7 [*C*CO(Q)], 122.9, 126.4, 126.5, 127.3, 133.8, 138.1 [4 × CH(Q), H*C*=CH], 146.6 [*C*N=C(Q)] and 160.5, 161.6 [CN(Q), CO(Q)]; *m*/*z*(%) 296 (MH$^+$, 100).

Aziridination of cyclohepta-1,3-diene with Q^{1}NHOAc 6–TTB

General aziridination procedure **B** was followed in this reaction using Q^{1}NH$_2$ **5** (200 mg, 0.81 mmol), LTA (396 mg, 0.89 mmol), TTB (576 mg, 1.69 mmol) and cyclohepta-1,3-diene (152 mg/0.18 cm^3, 2.96 mmol) in dichloromethane (5 cm^3). Work up in the normal way gave a light green solid which was crystallised from ethyl acetate–light petroleum giving *aziridine* **33** (79 mg, 29%) as a colourless solid, mp 173–174 °C. $[a]_D = +126.9$ ($c = 1.3$, EtOH) (Found: MH$^+$ 340.2025. C$_{20}$H$_{26}$O$_2$N$_3$ requires *M*H$^+$ 340.2026); ν_{max}/cm^{-1} 3490m, 1720s and 1580m; δ_H 1.02 [9H, s, C(CH$_3$)$_3$], 1.69–2.09 (4H, struct. m, 4 × C*H*), 2.30–2.45 (1H, m, C*H*), 2.77–2.88 (1H, m, C*H*), 2.90 (1H, dd, *J* 8.0, 4.8, azir. C*H*), 3.37 (1H, br ddd, *J* ~8, ~5, ~4, azir. C*H*), 3.77 (1H, d, *J* 10.4, CHO*H*), 5.08 (1H, d, *J* 10.4, C*H*OH), 6.01 (1H, ddd, *J* 11.9, 6.2, 2.0, C=C*H*CH$_2$), 6.10 (1H, ddd, *J* 11.9, 4.8, 2.5, NCHC*H*=C), 7.45 [1H, ddd, *J* 8.0, 6.9, 1.0, H-6(Q)], 7.64 [1H, dd, *J* 8.2, 1.0, H-8(Q)], 7.71 [1H, ddd, *J* 8.2, 6.9, 1.0, H-7(Q)] and 8.21 [1H, dd, *J* 8.0 1.0, H-5(Q)]; δ_C 23.1 (CH$_2$), 26.0 [C(*C*H$_3$)$_3$], 28.8, 31.7 (2 × CH$_2$), 38.4 [*C*(CH$_3$)$_3$], 52.4, 54.4 (2 × C-N), 74.5 (COH), 121.5 [*C*CO(Q)], 121.6, 126.3, 126.7, 126.9, 133.8 [4 × CH(Q), H*C*=CH], 139.5 (H*C*=CH), 144.7 [*C*N=C(Q)] and 157.6, 159.5 [CN(Q), CO(Q)]; *m*/*z*(%) 340 (MH$^+$, 100), 307 (78), 289 (39) and 215 (32). A crystal suitable for X-ray structure determination was obtained from methanol.

Aziridination of cycloheptatriene with Q^{2}NHOAc 11

General aziridination procedure **A** was followed in this reaction using 3-amino-2-isopropylquinazolin-4(3*H*)-one[11] (300 mg, 1.48 mmol), LTA (687 mg, 1.55 mmol), HMDS (597 mg, 3.69 mmol) and cycloheptatriene (272 mg, 0.29 cm^3, 2.96 mmol) in dichloromethane (6 cm^3) to give the crude product as a yellow oil. Column chromatography (4 : 1 light petroleum–ethyl acetate) gave *aziridine* **34** (193 mg, 45%), R_f 0.42, as a colourless oil which crystallised from ethyl acetate–light petroleum, mp 89–90 °C (Found: MH$^+$ 294.1606. C$_{18}$H$_{20}$ON$_3$ requires *M*H$^+$ 294.1606); ν_{max}/cm^{-1} 1660s and 1590s; δ_H 1.42 [6H, d, *J* 6.6, (CH$_3$)$_2$], 2.84 (1H, m, C*H*H), 2.99 (1H, dd, *J* 8.0, 3.7, azir. C*H*C=C), 3.03 (1H, ddd, *J* 15.6, ~5, ~5, C*H*H), 3.34 (1H, ddd, *J* ~8, ~7, 5.0, azir. C*H*CH$_2$), 3.63 [1H, heptet, *J* 6.6, C*H*(CH$_3$)$_2$], 5.89–6.08 (3H, struct. m, 3 × C=C*H*), 6.47 (1H, dd, *J* 11.0, 3.7, C=C*H*), 7.39 [1H, ddd, *J* 8.2, 6.6, 1.2, H-6(Q)], 7.58–7.68 [2H, m, H-7, H-8(Q)] and 8.17 [1H, dd, *J* 8.2, 1.0, H-5(Q)]; δ_C 21.1 [CH(*C*H$_3$)$_2$], 28.7 (CH$_2$), 30.8 [*C*H(CH$_3$)$_2$], 48.9, 58.3 (2 × C-N), 121.2 [*C*CO(Q)], 126.1, 127.0, 127.7, 127.8, 130.6, 130.9 [3 × CH(Q), 2 × H*C*=*C*H], 133.5 [CH(Q)], 146.1 [*C*N=C(Q)] and 160.1, 161.1 [CN(Q), CO(Q)]; *m*/*z*(%) 294 (MH$^+$, 100), 189 (39) and 173 (31).

Aziridination of cyclohexa-1,3-diene with Q^{2}NHOAc 11 in acetonitrile

A modification of general aziridination procedure **A** was followed using 3-amino-2-isopropylquinazolin-4(3*H*)-one (200 mg, 0.98 mmol), LTA (458 mg, 1.04 mmol), HMDS (397 mg, 2.46 mmol) and cyclohexa-1,3-diene (158 mg/0.18 cm^3, 1.97 mmol) in acetonitrile (4 cm^3). After work up the crude product was obtained as a yellow oil. Column chromatography (2 : 1 light petroleum–ethyl acetate) gave *alcohol* **30** (74 mg, 27%) as a colourless oil, R_f 0.88 (Found: MH$^+$ 300.1712. C$_{17}$H$_{22}$O$_2$N$_3$ requires *M*H$^+$ 300.1712); ν_{max}/cm^{-1} 3420m, 3300m, 1660s, 1615m and 1590s; δ_H 1.35 (3H, d, *J* 6.9, C*H*$_3$CHCH$_3$), 1.41 (3H, d, *J* 6.9, CH$_3$CHC*H*$_3$), 1.85 (1H, struct. m, C*H*), 2.05–2.37 (3H, m, C*H*$_2$C*H*H), 2.85 (1H, dddd, *J* ~10, ~10, ~3, ~3, C*H*NH), 3.64 [1H, heptet, *J* 6.9, C*H*(CH$_3$)$_2$], 3.96 (1H, br s, C*H*OH), 4.83 (1H, br s, OH), 5.78–5.87 (2H, struct. m, C*H*=C*H*), 5.93 (1H, d, *J* 10, NH), 7.46 [1H, ddd, *J* 8.0, 6.6, 1.3, H-6(Q)], 7.69–7.76 [2H, m, H-7, H-8(Q)] and 8.23 [1H, dd, *J* 8.0, 1.0, H-5(Q)]; δ_C(CDCl$_3$, 62.9 MHz) 20.5 (CH$_3$CH*C*H$_3$), 21.6 (CH$_2$), 21.8 (*C*H$_3$CHCH$_3$), 26.0 (CH$_2$), 30.8 [*C*H(CH$_3$)$_2$], 45.0 (C-N), 62.6 (C-OH), 119.8 [*C*CO(Q)], 126.5, 126.6, 127.4, 131.3, 134.5 [4 × CH(Q), H*C*=*C*H], 147.2 [*C*N=C(Q)] and 162.5, 163.4 [CN(Q), CO(Q)]; *m*/*z*(%) 300 (MH$^+$, 100), 282 (39), 204 (22), 189 (75) and 188 (50).

Further elution gave aziridine **20** (43 mg, 15%), R_f 0.57, as a colourless oil identical with that isolated previously and 2-isopropylquinazolin-4(3*H*)-one **31** (3 mg, 2%), R_f 0.22, as a colourless solid identical with an authentic sample.[11]

Aziridination of cyclohexa-1,3-diene with Q^{1}NHOAc 6–TTB in acetonitrile

A modification of general aziridination procedure **B** was followed using Q^{1}NH$_2$ **5** (500 mg, 2.01 mmol), LTA (942 mg, 2.12 mmol), TTB (1.42 g, 4.20 mmol) and cyclohexa-1,3-diene (320 mg/0.38 cm^3, 4.00 mmol) in acetonitrile (11 cm^3). After work up, column chromatography (6 : 1 light petroleum–ethyl acetate) gave dienylamine **24** (19 mg, 7%) as a colourless oil, R_f

0.26. Further elution gave aziridine **23** (101 mg, 38%) as a single diastereoisomer, R_f 0.21. The third fraction eluted, R_f 0.16, was a mixture which was re-chromatographed using Kieselgel (6 : 1 light petroleum–ethyl acetate) to give the major *(Q^1)-amino alcohol* diastereoisomer **27** (33 mg, 12%) as a colourless oil, R_f 0.19. $[a]_D$ +91.0 (c = 2.0, EtOH) (Found: MH^+ 344.1975. $C_{19}H_{26}O_3N_3$ requires MH$^+$ 344.1975); ν_{max}/cm^{-1} 3460s, 1660s, 1590s and 1470s; δ_H(400 MHz) 1.05 [9H, s, $(CH_3)_3$], 1.65 (1H, dddd, J ~13, ~7, ~3, ~3, C*H*HCN), 1.76 (1H, s, OH), 1.84 (1H, dddd, J 12.6, 11.9, 10.8, 5.0, CH*H*CN), 2.04 (1H, m, C=CC*H*H), 2.24 (1H, m, C=CCH*H*), 3.18 (1H, dddd, J ~12, ~8, ~3, ~3, C*H*NH), 3.62 (1H, br s, OH), 4.17 [1H, m, C*H*(OH)CN], 5.16 (1H, br d, J ~14, C*H*OH), 5.75–5.86 (2H, m, C*H*=C*H*), 5.90 (1H, d, J 7.6, NH), 7.50 [1H, ddd, J 8.2, 7.1, 1.2, H-6(Q)], 7.62 [1H, dd, J 8.2, 1.2, H-8(Q)], 7.72 [1H, ddd, J 8.2, 7.1, 1.0, H-7(Q)] and 8.27 [1H, dd, J 8.2, 1.0, H-5(Q)]; m/z(%) 344 (MH$^+$, 100) and 233 (42). Irradiation at δ 4.17 resulted in loss of J ~3 Hz from the signal at δ 3.18 and simplification of the C*H*=C*H* multiplet.

Further elution gave the minor *(Q^1)-amino alcohol* diastereoisomer **28** (17 mg, 6%) as a colourless oil, R_f 0.14. $[a]_D$ +113.3 (c = 1.2, EtOH) (Found: MH$^+$ 344.1975. $C_{19}H_{26}O_3N_3$ requires MH$^+$ 344.1975); ν_{max}/cm^{-1} 3420m, 1660s, 1595s and 1470m; δ_H(400 MHz) 1.05 [9H, s, $(CH_3)_3$], 1.80 (1H, dddd, J ~12.5, ~10, ~3, ~3, C*H*HCN), 1.92 (1H, dddd, J 12.5, 12.5, 8.5, 6.8, CH*H*CN), 2.19 (1H, struct. m, C*H*H), 2.31 (1H, struct. m, CH*H*), 2.96 (1H, dddd, J ~13, ~10, ~3, ~3, C*H*NH), 3.60 (1H, d, J 10.5, Bu^{t}CHO*H*), 3.93 [1H, br dd, J ~4, ~3, C*H*(OH)CN], 4.63 [1H, br d, J ~4, CH(O*H*)CN], 5.03 (1H, d, J 10.5, Bu^{t}C*H*OH), 5.79 (1H, dddd, J 9.9, ~5, ~1.5, ~1.5, C*H*=CCH$_2$), 5.84 (1H, d, J 10.0, NH), 5.90 (1H, ddd, J 9.9, ~5, ~3, C=C*H*CH$_2$), 7.55 [1H, ddd, J 8.2, 7.1, 1.2, H-6(Q)], 7.74 [1H, dd, J 8.0, 1.2, H-8(Q)], 7.83 [1H, ddd, J 8.0, 7.1, 1.2, H-7(Q)] and 8.30 [1H, dd, J 8.2, 1.2, H-5(Q)]; δ_C(75 MHz) 22.2, 26.2 (2 × CH$_2$), 26.3 [$(CH_3)_3$], 38.5 (CHNH), 62.6 (COH), 75.0 (CHOH), 120.5 [*C*CO(Q)], 126.5, 127.2, 127.6, 127.7, 131.6, 135.4 [4 × CH(Q), H*C*=*C*H], 146.3 [*C*N=C(Q)] and 158.8, 163.5 [CO(Q), CN(Q)]; m/z(%) 344 (MH$^+$, 100) and 233 (30).

Irradiation of the signal at δ 3.93 converted that at δ 4.63 into a singlet and that at δ 5.79 into a ddd J ~10, ~1.5, ~1.5 Hz, and that at δ 2.96 into a ddd J 13, 10 and 3.2 . Irradiation of the signal at δ 2.96 affected only that at δ 3.93 and CH_2 signals at δ 1.80 and 1.92.

Ring-opening of aziridine 23 with CH_3CN–H_2O–acid

Aziridine **23** (220 mg, 0.68 mmol) was stirred in acetonitrile (4 cm^3) containing water (1 cm^3) and toluene-*p*-sulfonic acid (8 mg) at ambient temperature for 2 h. Ethyl acetate (10 cm^3) was added, the solution washed with saturated sodium hydrogencarbonate solution (10 cm^3) and the organic layer separated, dried and evaporated. Column chromatography (7 : 1 light petroleum–ethyl acetate) of the residue gave *cyclic ether* **29** (53 mg, 24%) as a colourless oil, R_f 0.38. $[a]_D$ + 151.5 (c = 1.0, EtOH) (Found: MH$^+$ 326.1869. $C_{19}H_{24}O_2N_3$ requires MH$^+$ 326.1868); ν_{max}/cm^{-1} 1660s, 1600s, 1520m and 1470s; δ_H 1.30 [9H, s, $(CH_3)_3$], 1.92–2.37 (4H, m, 2 × CH$_2$), 3.23 (1H, struct. m, C*H*NH), 4.53 (1H, struct. m, HCO), 4.81 (1H, s, Bu^{t}C*H*O), 5.78 (1H, m, incl. J ~10, C*H*=CH), 6.06 (1H, struct. m, incl. J ~10, CH=C*H*), 6.60 (1H, br s, NH), 7.48 [1H, ddd, J 8.2, 5.3, 3.2, H-6(Q)], 7.69–7.76 [2H, m, H-7 and H-8(Q)] and 8.25 [1H, ddd, J 8.2, 1.2, H-5(Q)]; δ_C 20.8, 26.3 (2 × CH$_2$), 27.2 [$(CH_3)_3$], 34.9 [*C*(CH$_3$)$_3$], 56.2 (C-N), 74.4, 76.9 (2 × CHO), 120.4 [*C*CO(Q)], 126.6, 126.9, 127.2, 128.6, 132.4, 134.2 [4 × CH(Q), H*C*=*C*H], 146.7 [*C*N=C(Q)] and 154.1, 160.6 [CN(Q), CO(Q)]; m/z(%) 326 (MH$^+$, 100), 246 (30) and 215 (48).

Further elution gave the major alcohol diastereoisomer **27** (114 mg, 49%) R_f 0.27, and the minor diastereoisomer **28** (31 mg, 13%) R_f 0.14, both as colourless oils identical with those isolated previously.

Ring-opening of aziridine 23 in acetonitrile containing $H_2{}^{18}O$

Aziridine **23** (dr 5 : 1) (50 mg, 0.15 mmol) was dissolved in acetonitrile (1 cm^3) and $H_2{}^{18}O$ (8 µl, 2.5 equiv.) was added followed by toluene-*p*-sulfonic acid (~2 mg). After stirring for 45 min, ethyl acetate (10 cm^3) was added, the solution washed with saturated aqueous sodium hydrogencarbonate (10 cm^3) and the organic layer separated, dried, and evaporated. An NMR spectrum of the residue showed the presence of unchanged aziridine **23** (δ 3.58) and (Q^1)-amino alcohol **27** and **28** (δ 3.18 and 2.95; ratio 2 : 1 respectively) in a ratio of 4 : 1. For this mixture, mass spectrometry showed no ^{18}O incorporation into the aziridine (MH$^+$ 326). For the mixture of (Q^1)-amino alcohols **27** and **28** (Found: MH$^+$ 346.2016. $C_{19}H_{26}N_3{}^{16}O^{18}O$ requires MH^+ 346.2017) the ratio of 344 : 346 was 2 : 1. Separation of unchanged aziridine **23** and (Q^1)-amino alcohols **27** and **28** using flash silica [base-washed with triethylamine (2%) solution in light petroleum–ethyl acetate] and mass spectroscopy on the recovered alcohol **28** showed the ^{16}O : ^{18}O ratio was raised to 8 : 1. The recovered aziridine **23** (dr 14 : 1) was redissolved in acetonitrile (1 cm^3) and stirred for a further 2 h with $H_2{}^{18}O$ (5 µl, 2.5 equiv.) and toluene-*p*-sulfonic acid (~2 mg). After work up as described above, NMR spectroscopy showed the presence of alcohol **27** (Found: MH$^+$ 346.2017. $C_{19}H_{26}N_3{}^{16}O^{18}O$ requires MH$^+$ 346.2017) with a 344 : 346 ratio of 1 : 1 (10 : 1 after purification by flash chromatography).

Conversion of (Q^2)-amino alcohol 30 into oxazolidinone 36

(Q^2)-amino alcohol **30** (60 mg, 0.20 mmol) was heated under reflux in THF (1 cm^3) with sodium hydride (5 mg, 0.22 mmol) and 1,1′-carbonyldiimidazole (45 mg, 0.30 mmol) under nitrogen for 3 h. After cooling, ethyl acetate (10 cm^3) was added and the solution washed with saturated sodium hydrogencarbonate solution (10 cm^3), the organic layer was separated, dried and evaporated to give the crude product as a colourless solid. Column chromatography (5 : 1 light petroleum–ethyl acetate) gave unchanged alcohol **30** (21 mg, 35%) as a colourless oil, R_f 0.49.

Further elution gave *oxazolidinone* **36** (35 mg, 53%) as a colourless solid (R_f 0.33), mp 148–149 °C (from ethanol) (Found: MH$^+$ 326.1505. $C_{18}H_{20}O_3N_3$ requires MH$^+$ 326.1504); ν_{max}/cm^{-1} 1770s, 1680s and 1600s; δ_H 1.34 (3H, d, J 6.6, C*H*$_3$CHCH$_3$), 1.40 (3H, d, J 6.6, CH$_3$CHC*H*$_3$), 1.86 (2H, m, CH*H*), 2.08–2.21 (1H, m, C*H*H), 2.24–2.40 (1H, m, CH*H*), 3.18 [1H, heptet, J 6.6, C*H*(CH$_3$)$_3$], 4.02–4.15 (1H, m, NC*H*), 5.00–5.07 (1H, m, *H*CO), 6.00 (1H, m, incl. J 10.2, C*H*=CH), 6.26–6.35 (1H, m, incl. J 10.2, CH=C*H*), 7.45 [1H, ddd, J 8.0, 6.8, 1.4, H-6(Q)], 7.70 [1H, dd, J 8.2, 1.4, H-8(Q)], 7.77 [1H, ddd, J 8.2, 6.8, 1.1, H-7(Q)] and 8.22 [1H, dd, J 8.0, 1.1, H-5(Q)]; δ_C 20.2 (CH$_2$), 21.0 (CH$_3$), 22.8 (CH$_2$), 22.9 (CH$_3$), 30.6 [*C*H(CH$_3$)$_3$], 54.4 (N*C*HCH$_2$), 71.1 (C=CH*C*O), 121.4 [*C*CO(Q)], 123.2, 127.1, 127.3, 127.9, 133.3, 135.4 [4 × CH(Q), H*C*=CH], 147.4 [*C*N=C(Q)], 157.6, 159.9 and 163.4 [C=O, CN(Q), CO(Q)]; m/z(%) 326 (MH$^+$, 66), 307 (100) and 289 (50).

Conversion of (Q^1)-amino alcohol 27 into oxazolidinone 37

(Q^1)-amino alcohol **27** (37 mg, 0.11 mmol) was heated under reflux in THF (1 cm^3) with sodium hydride (3 mg, 0.12 mmol) and 1,1′-carbonyldiimidazole (22 mg, 0.14 mmol) under nitrogen for 3 h. After cooling, ethyl acetate (10 cm^3) was added and the solution washed with saturated sodium hydrogencarbonate solution (10 cm^3), the organic layer was separated, dried and evaporated to give the crude product as a colourless solid. Column chromatography (5 : 1 light petroleum–ethyl acetate) gave unchanged alcohol **27** (16 mg, 43%) as a colourless oil, R_f 0.18.

Further elution gave *oxazolidinone* **37** (20 mg, 49%) as a colourless oil, R_f 0.10. $[a]_D$ +39.5 (c = 1.0, EtOH) (Found: MH$^+$ 370.1766. $C_{20}H_{24}O_4N_3$ requires MH$^+$ 370.1767); ν_{max}/cm^{-1} 1790m, 1705m and 1605m; δ_H 0.99 [9H, s, $(CH_3)_3$], 1.67–1.86

(2H, m, CH_2), 2.00–2.24 (2H, m, CH_2), 3.32 (1H, d, *J* 10.8, CHO*H*), 4.12 (1H, ddd, *J* 11.6, 6.7, 4.6, NC*H*), 4.43 (1H, d, *J* 10.8, C*H*OH), 4.89–4.95 (1H, m, *H*CO), 5.93 (1H, dddd, *J* ~10, ~3, ~3, ~3, C*H*=CH), 6.18–6.27 (1H, m, CH=C*H*), 7.45 [1H, ddd, *J* 8.0, 6.9, 1.0, H-6(Q)], 7.62 [1H, dd, *J* 8.0, 1.0, H-8(Q)], 7.73 [1H, ddd, *J* 8.0, 6.9, 1.0, H-7(Q)] and 8.21 [1H, dd, *J* 8.0, 1.0, H-5(Q)]; *m*/*z*(%) 370 (MH^+, 100), 344 (22), 307 (25), 215 (28).

Conversion of (Q^1)-amino alcohol 28 into oxazolidinone 38

(Q^1)-amino alcohol **28** (23 mg, 67 μmol) was heated under reflux in THF (1 cm^3) with sodium hydride (2 mg, 73 μmol) and 1,1′-carbonyldiimidazole (16 mg, 0.10 mmol) under nitrogen for 3 h. After work up as described above, column chromatography (3 : 1 light petroleum–ethyl acetate) of the crude product gave alcohol **28** (11 mg, 48%) as a colourless oil, R_f 0.24.

Further elution gave *oxazolidinone* **38** (11 mg, 44%) as a colourless oil, R_f 0.19 (Found: MH^+ 370.1766. $C_{20}H_{24}O_4N_3$ requires *M*H^+ 370.1767); ν_{max}/cm^{-1} 1790 m, 1695 m and 1605 m; δ_H 1.06 [9H, s, $(CH_3)_3$], 1.85–2.00 (2H, m, 2 × C*H*), 2.10–2.27 (1H, m, C*H*H), 2.37–2.54 (1H, m, C*H*H), 2.95 (1H, d, *J* 11.2, CHO*H*), 4.54 (1H, ddd, *J* ~8, ~4, ~4, NC*H*), 4.71 (1H, d, *J* 11.2, C*H*OH), 5.23–5.31 (1H, m, *H*CO), 5.89 (1H, dddd, *J* 13.1, ~3, ~3, ~2, C*H*=C), 6.18–6.27 (1H, m, C=C*H*), 7.52 [1H, ddd, *J* 8.2, 6.8, 1.1, H-6(Q)], 7.70 [1H, dd, *J* 8.2, 1.1, H-8(Q)], 7.82 [1H, ddd, *J* 8.2, 6.8, 1.1, H-7(Q)] and 8.27 [1H, dd, *J* 8.2, 1.1, H-5(Q)]; δ_C(75 MHz) 20.3, 21.9 (2 × CH_2), 26.3 [$(CH_3)_3$], 37.2 [*C*$(CH_3)_3$], 70.9, 74.7 (2 × *C*H), 121.7 [*C*CO(Q)], 122.8, 127.7, 127.9, 128.0, 133.2, 135.7 [4 × CH(Q), H*C*=*C*H], 146.2 [*C*N=C(Q)], 157.2 [OC(O)N] and 159.0, 159.6 [CN(Q), CO(Q)]; *m*/*z*(%) 370 (MH^+, 100). A COSY spectrum showed the signal at δ 1.85–2.00 (CH_2) coupled with δ 4.54 (NC*H*) and δ 5.89 (C*H*=CCH_2) coupled with δ 5.23–5.31 (*H*CO).

Q^1–N reductive cleavage of oxazolidinone 37 with Sm(II) iodide[10]

A two-necked round bottom flask fitted with a 3-way tap and a septum cap was flame dried, flushed with argon and oxazolidinone **37** (17 mg, 45.9 μmol) dissolved in THF (1 cm^3) was added *via* a syringe followed by *tert*-butyl alcohol (0.5 cm^3) in THF (0.5 cm^3). Samarium(II) iodide (0.1 M solution in THF) was then added dropwise until the dark blue colour of samarium(II) persisted (~1 cm^3). Ethyl acetate (5 cm^3) was added and the solution washed with saturated sodium hydrogencarbonate solution (5 cm^3), the organic layer was separated, dried and evaporated to give the crude product as a yellow semi-solid. Column chromatography (6 : 1 light petroleum–ethyl acetate) gave a mixture of products. Subsequent Kieselgel chromatography (9 : 1 ethyl acetate–methanol) gave quinazolin-4(3*H*)-one **40** (8 mg, 75%) as a colourless crystalline solid, identical with a sample isolated previously.[5]

Further elution gave *oxazolidinone* **39** (4 mg, 62%) as a colourless solid, mp 85–86 °C (from light petroleum–ethyl acetate) [lit.[13] (racemate) 86–88 °C]. $[\alpha]_D$ −10.6 (*c* = 0.5, EtOH) (Found: MH^+ 140.0711. $C_7H_9O_2N$ requires *M*H^+ 140.0712); ν_{max}/cm^{-1} 3220m and 1740m; δ_H 1.70–1.78 (1H, m, C*H*), 1.80–2.05 (2H, m, 2 × C*H*), 2.15–2.31 (1H, m, C*H*), 3.89–4.03 (1H, struct. m, C*H*NH), 4.87–4.95 (1H, m, *H*CO), 5.07 (1H, br s, NH), 5.79–5.88 (1H, m, C*H*=CH) and 6.11–6.22 (1H, m, CH=C*H*); *m*/*z*(%) 162 (MNa^+, 100) and 140 (MH^+, 67).

Q^1–N reductive cleavage of oxazolidinone 38 with Sm(II) iodide[10]

The procedure described above was carried out using oxazolidinone **38** (11 mg, 29.7 μmol), and *tert*-butyl alcohol (0.5 cm^3) in THF (1 cm^3). Samarium(II) iodide (0.1 M solution in THF) was added dropwise until the dark blue colour of samarium(II) metal persisted (~0.8 cm^3). After work up column chromatography (6 : 1 light petroleum–ethyl acetate) of the yellow residue gave a mixture of products. Subsequent Kieselgel chromatography (9 : 1 ethyl acetate–methanol) gave quinazolin-4(3*H*)-one **40** (5 mg, 72%), R_f 0.71, as a colourless crystalline solid identical to that isolated previously.

Further elution gave oxazolidinone **enant. 39** (2.5 mg, 60%) as a colourless solid, mp 87–88 °C (from light petroleum–ethyl acetate). $[\alpha]_D$ +13.2 (*c* = 0.5, EtOH) (Found: MH^+ 140.0711. $C_7H_9O_2N$ requires *M*H^+ 140.0712); ν_{max}/cm^{-1} 3220m and 1740m; NMR spectrum identical to that of **39** above; *m*/*z*(%) 162 (MNa^+, 100) and 140 (MH^+, 67).

Crystal structure determinations of 21 and 33

Data for both compounds were measured on a Siemens P4 diffractometer with graphite monochromated Mo-Kα radiation (λ = 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.

The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the program SHELXL-97. All hydrogen atoms were included in calculated positions (C–H = 0.96 Å) using a riding model. All non-hydrogen atoms were refined as anisotropic. The absolute configuration of 33 at C1 is determined by the preparation from the (*S*)-*tert*-leucine.

Crystal data for 21. $C_{15}H_{12}F_3N_3O$, *M* = 307.28, monoclinic, space group *C*2/*c*, *a* = 24.012(3), *b* = 7.609(1), *c* = 15.758(2) Å, β = 105.89(1)°, *V* = 2769.1(6) $Å^3$, *T* = 200 K, *Z* = 8, μ(Mo-Kα) = 0.123 mm^{-1}, colourless block, crystal dimensions 0.49 × 0.21 × 0.20 mm. Full matrix least squares based on F^2 gave *R*1 = 0.070 for 808 observed data ($F > 4\sigma(F)$) and *wR*2 = 0.232 for all 1038 data, GOF = 1.078 for 145 parameters.

Crystal data for 33. $C_{20}H_{25}N_3O_2$, *M* = 339.43, tetragonal, space group $P4_3$, *a* = *b* = 10.242(2), *c* = 17.385(3) Å, *V* = 1823.7(6) $Å^3$, *T* = 200 K, *Z* = 4, μ(Mo-Kα) = 0.08 mm^{-1}, colourless block, crystal dimensions 0.62 × 0.48 × 0.41 mm. Full matrix least squares based on F^2 gave *R*1 = 0.036 for 1579 observed data ($F > 4\sigma(F)$) and *wR*2 = 0.097 for all 1779 data, GOF = 1.030 for 226 parameters.

Acknowledgements

We thank Dr J. Fawcett and Dr D. R. Russell for the X-ray crystal structure determinations.

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