Intramolecular Reactions of *N*-Nitrenes with Alkynes: Conformational Anchoring in Spiro-fused 2*H*-Azirines

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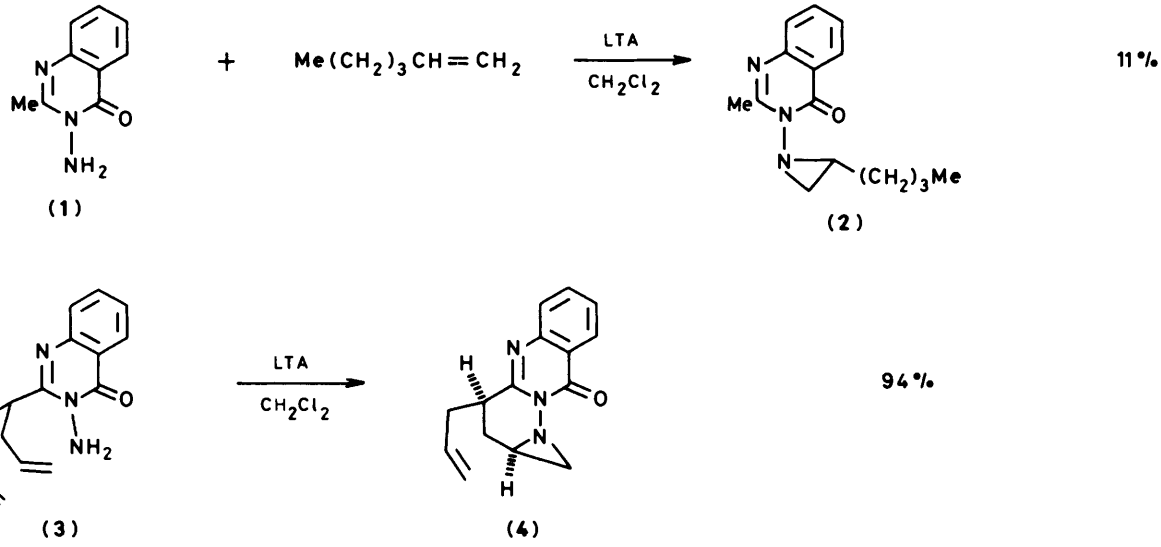
Oxidation of *N*-aminoquinazolin-4(3*H*)-ones (**7**)—(**11**) with lead tetra-acetate in dichloromethane results in the intramolecular addition of the *N*-nitrene to the triple bond in each case and azirines (**20**), (**22**), (**17**), (**23**), and (**30**), respectively, are isolated with (**31**) identified as a by-product in the oxidation of compound (**11**). An *X*-ray crystal structure determination on compound (**17**) reveals a remarkable deformation of bond angles at the spiro centre and this feature appears to be common to all azirines. The five membered ring in the azirines (**17**), (**20**), (**22**), and (**23**) has the envelope conformation (**26**) and the six-membered ring in azirine (**30**) has the twist-boat conformation (**32**): a possible explanation for this conformational anchoring is offered.

Our studies of the reactions of *N*-nitrenes have shown that poor traps for these species can be much improved by carrying out the trapping intramolecularly.[1,2] Thus oxidation of the 3-amino-2-methyl quinazolone (**1**) in the presence of a terminal alkene *e.g.* hex-1-ene, gave the aziridine (**2**) in only 11% yield whereas oxidation of the *N*-aminoquinazolone (**3**) gave the corresponding aziridine (**4**) in 94% isolated yield.

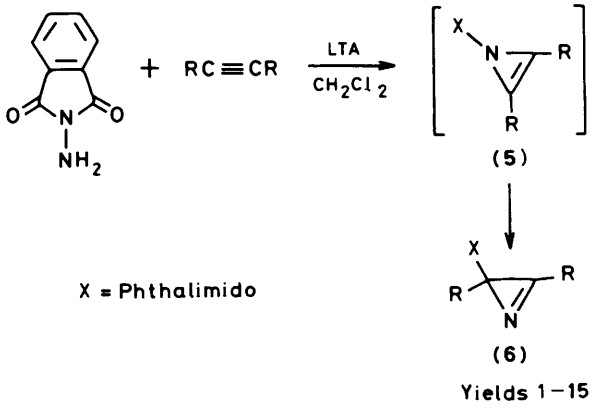


Alkynes are also poor traps in intermolecular reactions with *N*-nitrenes and low yields of the (rearrangement) products (**6**) (Scheme 1) are isolated from the oxidation of *N*-aminophthalimide in the presence of dialkylalkynes.[3] Our attempts to trap the *N*-nitrene from oxidation of the *N*-aminoquinazolone (**1**) by hex-1-yne were unsuccessful and no product analogous to compound (**6**) was isolated. We have examined the intramolecular version of this reaction with the expectation of increasing the efficiency of trapping. It was hoped also that the intramolecular reaction might permit observation or identification of the proposed transitory 1*H*-azirines (**5**) (Scheme 1) which are believed to rearrange rapidly to the isolated 2*H*-azirines (**6**).[3]

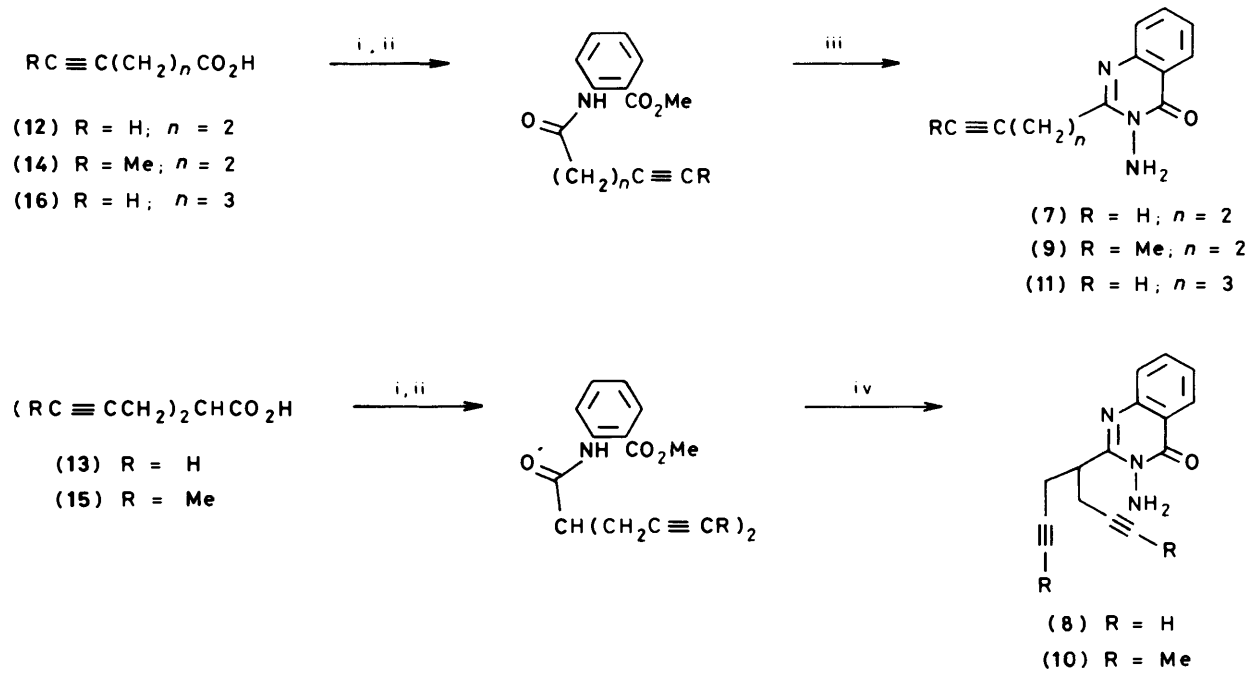
The 2-(alkynylalkyl)-3-aminoquinazolones (**7**)—(**11**) were synthesised from the corresponding acids (**12**)—(**16**) in the usual way (Scheme 2).

The acids (**12**)—(**15**) were obtained by mono- or di-alkylation of malonate esters with the appropriate alkynyl bromide or toluene-*p*-sulphonate followed by hydrolysis and decarboxylation: the acid (**16**) was obtained by chain extension of the acid (**12**) (Scheme 3).

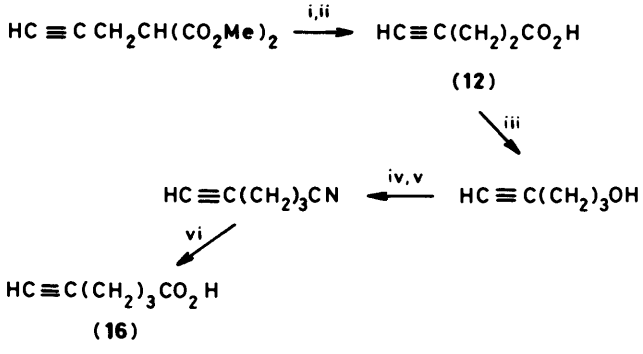
The oxidations of compounds (**7**)—(**11**) were carried out by slow and simultaneous addition of the *N*-aminoquinazolone and lead tetra-acetate (LTA) as solutions in dry dichloro-



Scheme 1.



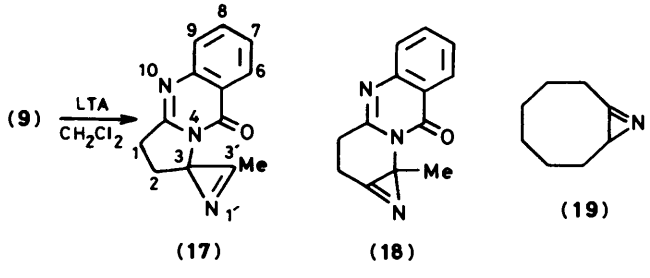
Scheme 2. *Reagents:* i, $SOCl_2$; ii, methyl anthranilate; iii, NH_2NH_2–EtOH; iv, NH_2NH_2–EtOH, 120 °C (sealed tube).

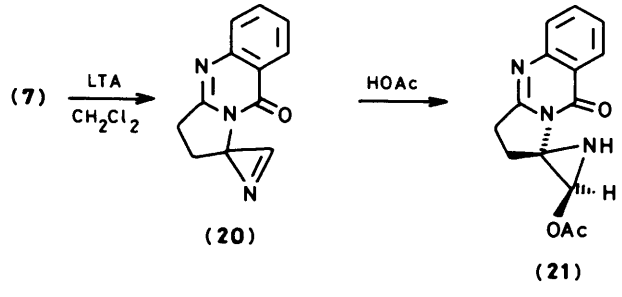


Scheme 3. *Reagents:* i, NaOH–EtOH; ii, 160 °C; iii, $LiAlH_4$; iv, TsCl–pyridine; v, KCN–DMSO; vi, NaOH–water.

methane in different separating funnels to stirred dry dichloromethane. In the oxidation of compound (**9**), a crystalline product was obtained in quantitative yield after separating the lead diacetate, washing the dichloromethane solution with aqueous sodium hydrogen carbonate, and then evaporating this dried solution. The spectroscopic data for this oxidation product were in agreement with its formulation as the spiro-azirine (**17**). Although the alternative isomer (**18**) was compatible with this data, bicyclo[*n*.1.0] ring fused azirines have been previously isolable only $n \geqslant 6$ *e.g.* (**19**).[4]

Confirmation of the structure of this oxidation product as (**17**) was eventually obtained by carrying out an *X*-ray crystal structure determination[5] (see below) but meanwhile, a similar oxidation of compound (**7**) gave a product whose spectroscopic data unambiguously supported (**20**) as its structure.



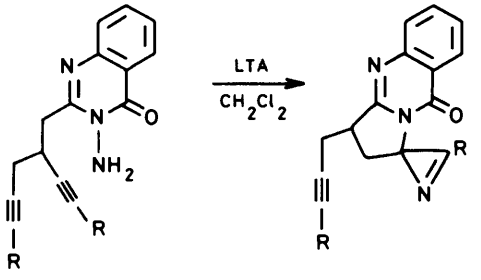


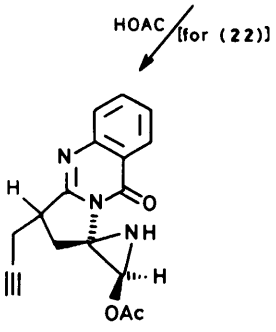
Thus compound (**20**) shows a characteristic low-field resonance at δ 10.41 (*J* 2.8 and 0.6 Hz) for the azirine ring proton. Coupling of the azirine ring protons at C-3 over four bonds has been previously reported[6] but it is clear that only one of the methylene protons adjacent to the spiro-centre in (**20**) is significantly coupled in this way, *i.e.* the magnitude of the coupling is dependent on geometrical factors. The C=N azirine stretching frequency in the i.r. spectrum of compound (**17**) was apparent as a weak band at 1 785 cm^{-1}. No band of even weak intensity is observed in this position in the i.r. spectrum of (**20**) [or other azirines bearing hydrogen at C-3 (azirine) reported below] and this has been noted previously for azirines unsubstituted at C-3.[6]

The azirine (**20**) is more reactive than (**17**) and the yield of this product was maximised when contact with acetic acid (a by-product of the oxidation using LTA) in the reaction medium

was minimised: if work-up was carried out after setting the reaction mixture aside overnight the only product isolated was the acetic acid addition product (**21**). Addition of acetic acid or formic acid to the azirine (**20**) in more concentrated solution was very rapid and could be readily monitored by n.m.r. spectroscopy by gradual addition of either of these acids in small quantities (as solutions in deuterio-chloroform) to deuteriochloroform solutions of the azirine (**20**). By contrast, the azirine (**17**) was markedly less reactive towards acetic acid and no measurable loss of signals from this azirine in its n.m.r. spectrum was apparent after several hours in contact with two mol equiv. of acetic acid in chloroform solution. This lesser reactivity of (**17**) suggests that addition of acetic acid does not proceed *via* initial protonation of the azirine ring nitrogen with the generation of a carbonium ion as an intermediate.

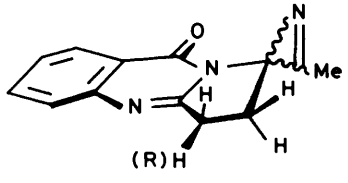
Oxidation of the *N*-aminoquinazolones (**8**) and (**10**) bearing bifurcated chains also proceeded in excellent yield to give the corresponding azirines (**22**) and (**23**). Like the C-3 unsubstituted azirine (**20**), (**22**) is also very reactive towards the acetic acid generated in its formation. The addition product (**24**) which



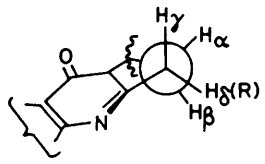


(**24**)

results is assigned the stereochemistry shown at the acetoxy-bearing carbon [as is the case with (**21**)] with the assumption of attack by acetic acid from the side of the azirine ring opposite to the quinazolone.



(**25**)



	$J\alpha\gamma$	$J\alpha\delta$	$J\beta\gamma$	$J\beta\delta$
(**17**)	9.3	1.3	10.9	9.6
(**20**)	8.1	—	10.6	—
(**22**)	9.3	1.5	10.9	9.7
(**23**)	8.3	—	10.5	—

Figure 1. Approximate Newman projection along the CH_2–CH_2-(CHR–CH_2) bond in azirines (**17**), (**20**), (**22**), and (**23**) as deduced from the vicinal coupling constants (in Hz) in their n.m.r. spectra as indicated.

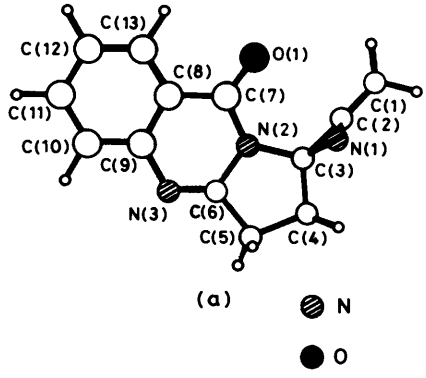


Figure 2. *X*-Ray crystal structure of the azirine (**17**).

Comparison of the n.m.r. spectra of the azirines (**17**), (**20**), (**22**), and (**23**), showed clearly that they all had the same conformation for the five-membered ring whose envelope shape (**25**) accorded with the magnitude of the vicinal coupling constants between the five-membered ring protons as shown in the Newman projection along the CH_2–CH_2 [$CH(R)$–CH_2] bond (Figure 1). The orientation of the azirine ring with respect to the envelope flap was, at this stage, unknown.

Although these assignments were self-consistent, it was not obvious to us why the five-membered ring should apparently have a conformational preference for the envelope flap to be located on one side rather than the other of the plane containing the quinazolone ring. The two sides of the quinazolone ring in compounds (**17**) and (**20**) are defined by the orientation of the azirine ring and it was logical to assume that the origin of the conformational preference of the five-membered ring was to be found in a corresponding preference of the C–N (or C–C) bond of the azirine ring for one of the two differentiated positions on the five-membered ring at the spiro-centre.

An *X*-ray structure determination was carried out on the azirine (**17**) and gave the result shown in Figure 2.* More informative is a view of the spiro ring-fusion from a direction orthogonal to the azirine ring (Figure 3) with the remnant of the quinazolone ring removed for clarity.

* Figure 2 differs from the same Figure in our original communication in that a hydrogen atom in the latter on the carbon atom of the 5-membered ring adjacent to the spiro centre (C-4) was inadvertently drawn in when in fact it is not visible from the perspective drawn.

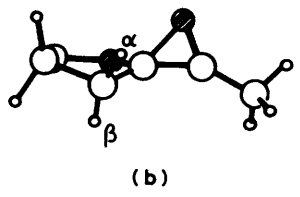


Figure 3. *X*-Ray crystal structure of azirine (**17**) viewed perpendicularly to the azirine ring with the quinazolone ring residue removed for clarity.

long C–N bond in azirines has been ascribed to high p-character in the C-2 derived component of this bond.[10]

Our analysis of the n.m.r. spectrum of compound (**17**) [together with compounds (**20**), (**22**), and (**23**)] is in agreement with the same geometry at the spiro-centre in solution as in the crystal structure. In particular, the chemical shift upfield of the signal from H_α (Figure 3) by comparison with H_β (δ 1.75 versus 2.65, respectively) can be ascribed to shielding of H_α by the adjacent azirine ring.[12,†] However, there remains the problem of why conformation (**26**) is preferred over (**27**) for these five-membered ring spiro-fused azirines. Both these conformations

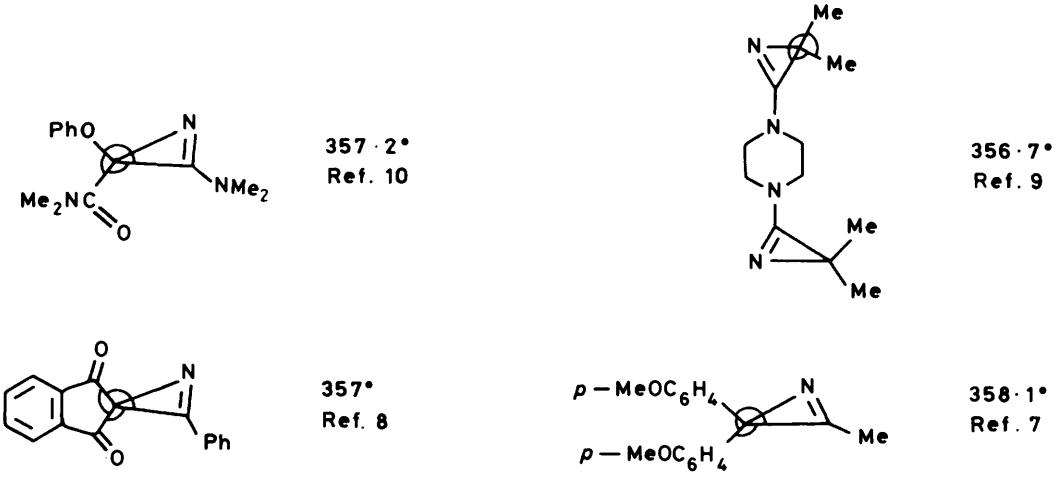
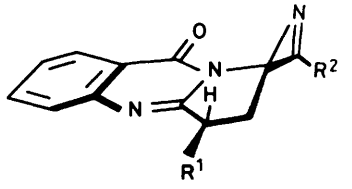


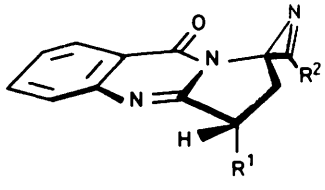
Figure 4. (Metal free) Azirine ring containing crystal structures retrieved from the Cambridge crystallographic data file with the reported angle summations at C-2 indicated.

From this viewpoint it can be seen that the C–C bond of the azirine ring is close to the plane defined by the C–N and C–C bonds of the five-membered ring to the spiro-centre: in fact the C–C and C–N bonds of the azirine ring have angles of 5.9° and 45.9°, respectively, to this plane. Alternatively, the near-coplanarity of C–N and C–C bonds of the five-membered ring and the C–C bond of the azirine ring can be quantified by summation of the angles between them which gives a value of 358 ± 1.2°: a perfect plane would, of course, require a value of 360°.

This unexpected feature of the azirine ring geometry in compound (**17**) was the more surprising when it was found to be also present, but unremarked upon, in the four azirine ring-containing crystal structures[7,8,9,10] available from the Cambridge Data File. The appropriate angle summations in these four structures are shown in Figure 4 and it is clear that the substantial deformation towards coplanarity at C-2 as in (**17**) has taken place in all cases. This deformation at C-2 in (presumably all) azirines can be accommodated by assuming hybridisation for the carbon atom at this position which is close to sp^2 with the C–N bond of the azirine formed by overlap of the p-orbital at C-2 with the nitrogen hybrid orbital. In fact, sp^2-hybridisation for C-2 in azirines has been suggested by Hassner[11] to account for the particular value of the ^{13}C–H coupling constant at this position.* In addition, the abnormally



(**26**)

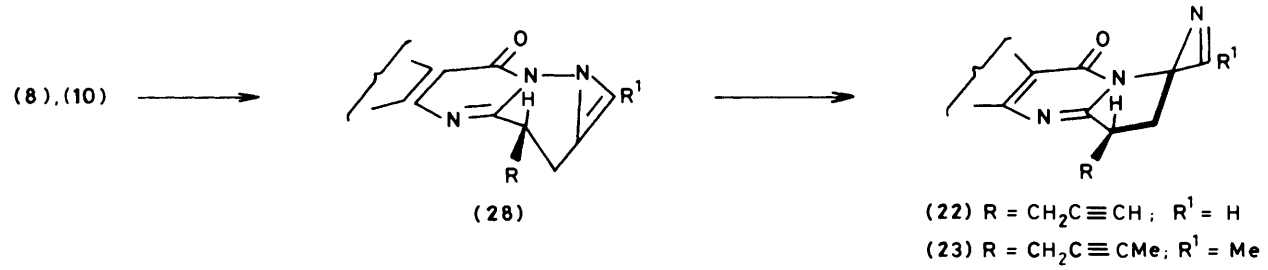


(**27**)

have the azirine C–C bond close to the plane containing the two five-membered ring bonds to the spiro-centre and they are interconverted by movement of the envelope flap from one side to the other. Of course, in the ring-substituted compounds (**22**) and (**23**) there may be a contribution to the stabilisation of (**26**) over (**27**) from the preferred siting of the side-chain R in an 'equatorial' rather than an 'axial' position but (**17**) and (**20**) are free from this complication and yet still have the same preferred conformation for the five-membered ring. An examination of models of (**26**) and (**27**) suggests that the origin of the greater stability of (**26**) may be the result of an alignment of the (bonded) p-orbital at the spiro-centre in the latter with the filled p-orbital of the quinazolone ring nitrogen. The tilting of the p-

* Hassner has also suggested that both C-3 and N or the azirine ring have sp-hybridisation.

† Exactly which part of the azirine ring brings about this shielding is not clear.

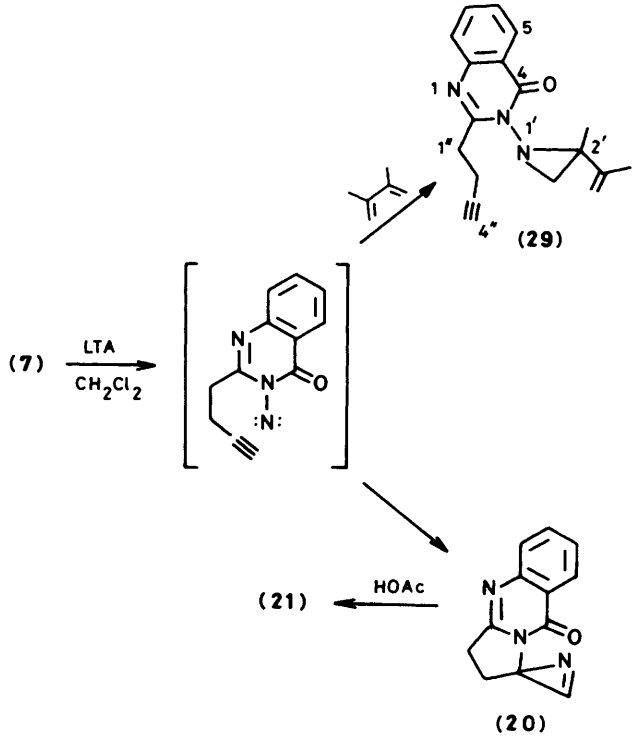


orbital at the spiro-centre which is anticipated (if only because the three bonds to the spiro-centre referred to earlier are not completely coplanar) would serve to improve this alignment in (**26**) but to reduce it in (**27**).

The stereospecific formation of (**22**) and (**23**) with the side-chain and C–N bond of the azirine ring *trans* is of interest. If the addition of the nitrene to the triple bond resembles the corresponding intramolecular addition to a double bond,[1] then the rigid boat-shaped 6-membered ring 1*H*-azirine intermediate (**28**) results.

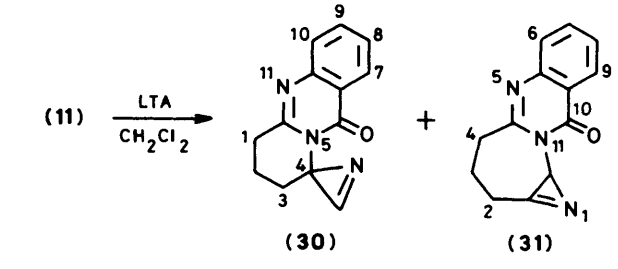
[1,2]-Migration of the N–N bond in this 1*H*-azirine delivers (**22**) and (**23**) *directly* in their stable conformations [*cf.* (**26**)]. Although the envelope conformations (**26**) of azirines (**17**), (**20**), (**22**), and (**23**) would, therefore, be the kinetically favoured products of rearrangement, it is likely that they are also the thermodynamically favoured conformations since the n.m.r. spectrum of compound (**17**) in chlorobenzene was unchanged when recorded at 120 °C.

Our attempts to trap the 1*H*-azirines have not proved successful. Oxidation of 3-aminoquinazolone (**7**) at −78 °C under our conditions proceeds very slowly if at all. Addition of a large excess of 2,3-dimethylbutadiene to the solution at this low temperature and then allowing the temperature to rise slowly to ambient with vigorous stirring gave the aziridine (**29**) and, significantly, some of the azirine (**20**) together with its acetic acid addition product (**21**) (Scheme 4). Clearly the nitrene is intercepted for the most part by the diene but the formation of the azirine (**20**) in the same reaction mixture indicates that either the 1*H*-azirine to 2*H*-azirine rearrangement is very fast or that the 1*H*-azirine is not particularly reactive towards 2,3-dimethylbutadiene.



Scheme 4.

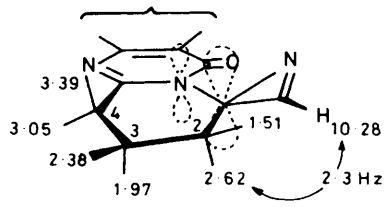
Oxidation of the *N*-aminoquinazolone (**11**) was carried out as described previously for compounds (**7**)—(**10**) and an n.m.r. spectrum of the crude reaction product revealed that a mixture of the azirines (**30**) and (**31**) was present in a 9:4 ratio, respectively. Crystallisation from methanol gave a pure sample of (**30**). Interestingly, the azirine (**30**) was significantly more resistant towards attack by acetic acid than its spiro-fused five-membered ring analogues (**20**) and (**22**) and none of the acetic acid addition product [analogous to (**21**)] was isolated; n.m.r. monitoring of the solution showed that the mixture of (**30**) and (**31**) was stable to two mol equiv. of acetic acid in deuteriochloroform over several hours.



Analysis of the n.m.r. spectrum of (**30**) shows that it is present in solution in the single skew boat conformation (**32**). This conclusion follows from the vicinal coupling constants in the trimethylene unit and assumes the same near coplanarity of the azirine C–C bond and the two six-membered ring bonds at the spiro-centre. The spatial relationship of the protons on the carbon (C-2) adjacent to the spiro-centre *vis-à-vis* the azirine ring is very similar to the situation in (**20**) (*cf.* Figure 3) with a higher field proton (δ 1.51 versus 1.75) and a lower field proton (δ 2.62 versus 2.65), the latter coupled in both cases to the azirine ring proton (*J* 2.3 versus 2.8 Hz, respectively).

Newman projections looking along the C(3)–C(2) and C(3)–C(4) bonds in (**32**) are represented in Figure 5 with the vicinal coupling constants as shown. The magnitude of these vicinal coupling constants for C(2)H–C(3)H excludes half-chair conformations for (**30**) *e.g.* (**33**) since none of them is large enough for an axial-axial coupling (*ca.* 12 Hz). Although the coupling constants in Figure 5 are compatible with the alternative skew-boat (**34**), this conformation has a different Newman projection along the C(2)–C(spiro) bond to those of (**32**) and (**20**) Figure (**6**) and the chemical shift of the methylene proton signals at C-2 and, in particular, the coupling constant of the azirine ring H to the lower field proton would not be expected to be so similar for conformations (**34**) and (**20**).

Why should the skew-boat (**32**) be favoured to the exclusion



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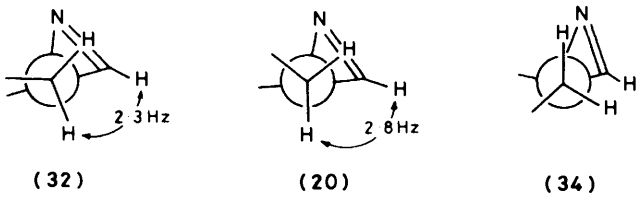
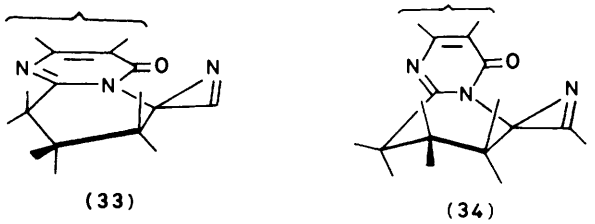
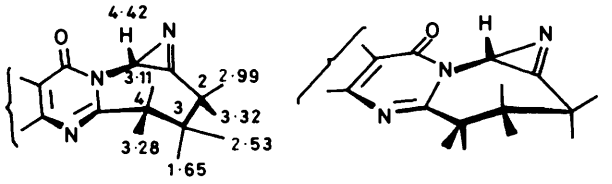


(32) (20) (34)

Figure 6. Approximate Newman projections along the C(2)–C(spiro) bonds in compounds (**32**), (**20**), and (**34**) [the alternative skew boat conformation of (**32**)] as drawn from models.



(33) (34)



(35) (36)

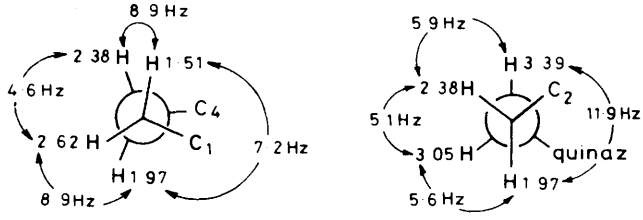


Figure 5. Approximate Newman projections along the C(2)–C(3) and C(3)–C(4) bonds in the azirine (**32**) as deduced from the vicinal coupling constants (in Hz) in its n.m.r. spectrum as indicated.

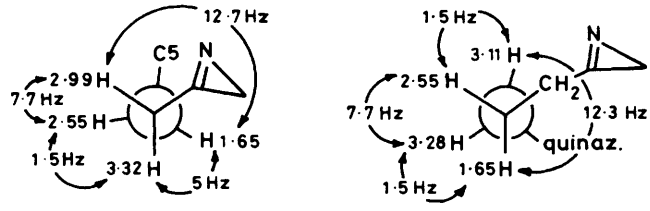
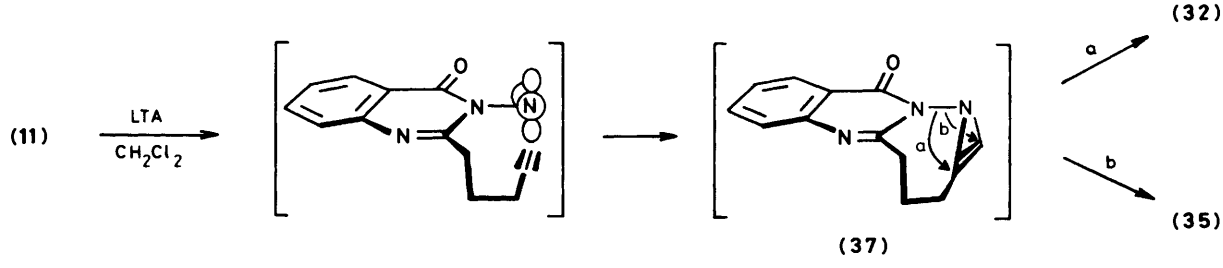
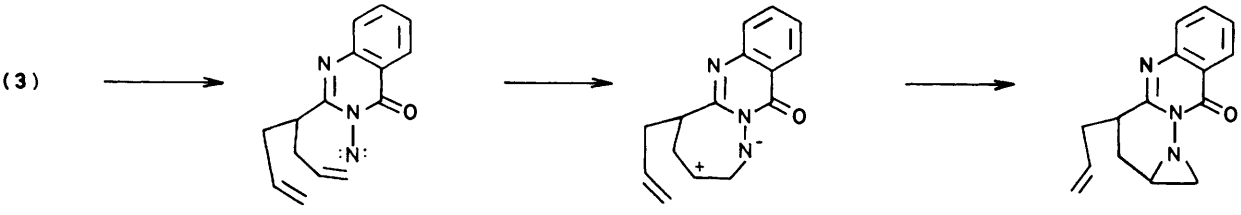


Figure 7. Approximate Newman projections along the C(3)–C(4) and C(4)–C(5) ring bonds of the azirine (**31**) as deduced from the vicinal coupling constants (in Hz) in its n.m.r. spectrum as indicated.



Scheme 5.



Scheme 6.

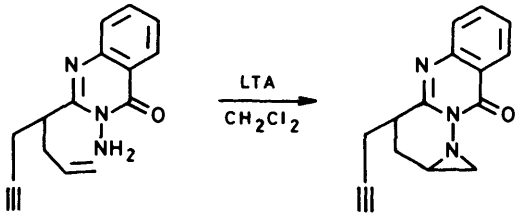
of other conformations? An examination of models suggests that, as in the case of (**26**), it is in conformation (**32**) that the p-orbital at the spiro-centre may have the best alignment with the adjacent p-orbital of the quinazolone nitrogen [see (**32**)].

The ring-fused azirine (**31**) has not been separated from (**30**) but in the 400 MHz spectrum of the mixture, signals from compound (**31**) are sufficiently separated from those of (**30**) for the structure of the former to be assigned. Thus the azirine ring proton signal is a singlet at δ4.42 and the vicinal coupling constants within the trimethylene chain show the ring to have the conformation shown in (**35**). Figure 7 shows Newman projections along the C(2)–C(3) and C(3)–C(4) bonds with the measured vicinal coupling constants. Models of (**31**) suggest that besides (**35**) there is an alternative conformation (**36**) for

this ring-fused azirine in which there is even better staggering of bonds in the trimethylene chain but which, nevertheless, is incompatible with the vicinal coupling constants in Figure 7.*

By analogy with the intramolecular addition of *N*-nitrenes to alkenes,[1] the addition of the nitrene derived by oxidation of (**11**) to the alkyne bond would be expected to lead to the conformation of the 1*H*-azirine indicated in Scheme 5. Migration of the N–N bond in the 1*H*-azirine (**37**) as indicated leads *directly* to compounds (**30**) and (**31**) in the conformations in which they are shown [(**32**) and (**35**), respectively] [*cf.* the rearrangement of (**28**)].

In the oxidation of 2-alkenylethyl-3-aminoquinazolones *e.g.* (**3**), intramolecular addition of the nitrene was believed to take place *via* a transition state having dipolar character (Scheme 6).[1] In the oxidation of compound (**38**), only the aziridine (**39**),



(**38**) (**39**) 84%

from addition of the *N*-nitrene to the alkene was isolated (84%). This preference for attack on the double bond by the nitrene can be rationalised in terms of the lesser stability of the partial vinyl cation which would result from electrophilic attack of the nitrene on the triple bond.

Experimental

N.m.r. spectra refer to those run at 90 MHz unless otherwise indicated. I.r. spectra were run as Nujol mulls on a Perkin-Elmer 298 spectrophotometer. Prop-2-ynyl bromide was purchased as an 80% solution in toluene (Aldrich) and was used as received. But-2-yn-1-yl toluene-*p*-sulphonate was prepared from but-2-yn-1-ol (Aldrich) and toluene-*p*-sulphonyl chloride using the method of Brandsma.[13] But-2-ynyl bromide was obtained by treatment of the corresponding alcohol with phosphorus tribromide.[14] Lead tetra-acetate was freed from acetic acid prior to use by placing in a vacuum desiccator and evacuating using a water-pump for 5 min. Dichloromethane was distilled prior to use by distillation from calcium hydride.

Dimethyl Disubstituted Propanedioates $R_2C(CO_2Me)_2$.—These were prepared by reaction of the sodium salt of dimethyl malonate with prop-2-ynyl bromide or 1-bromobut-2-yne in dry methanol followed by successive addition of a further mol equiv. of sodium methoxide and an additional mol equiv. of an alkylating agent. The following esters were prepared in this way: *Dimethyl 2,2-dibut-2-ynylpropan-1,3-dioate* (using 1-bromobut-2-yne). A colourless solid (81%), m.p. 53—55 °C (from ethyl acetate–light petroleum) (Found: C, 66.0; H, 6.8. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8%); δ 3.68 (s, CO_2Me), 2.84 (q, *J* 2 Hz, CH_2), and 1.70 (t, *J* 2 Hz, Me); Dimethyl 2,2-diprop-2-ynylpropane-1,3-dioate (using prop-2-ynyl bromide). A colourless solid (81%), m.p. 85—87 °C (from ethyl acetate–light petroleum) (lit.,[15] m.p. 87—88 °C). Dimethyl 2-(prop-2-enyl)-2-(prop-2-ynyl)propane-1,3-dioate was prepared similarly by reaction of dimethyl 2-(prop-2-enyl)propane-1,3-dioate, $H_2C{=}CHCH_2CH(CO_2Me)_2$[16] with prop-2-ynyl bromide and was obtained as a colourless liquid (78%), b.p. (Kugelrohr) 120—123 °C/14 mmHg; δ 5.58 (m, $CH{=}CH_2$), 5.16 (m, $CH{=}CH_2$), 3.78 (s, 2 × CO_2Me), 2.62 (m, 2 × CH_2), and 2.02 (t, *J* 2.5 Hz, C≡C*H*); $\nu_{max.}$ 3 345w, 3 000w, 1 760s, 1 450m, 1 305m, 1 240s, and 940w cm^{-1}.

Dimethyl Monosubstituted Propanedioates $RCH(CO_2Me)_2$.—These were prepared as above by reaction of the sodium salt of dimethyl malonate with prop-2-ynyl bromide or but-2-yn-1-yl toluene-*p*-sulphonate (1 mol equiv.) in dry methanol but in both cases substantial di-substitution occurred. The mixture for the case of R = $CH_2C{\equiv}CH$ (ratio mono:disubstitution 2.3:1) was partially separated in the following way: to its solution in methanol was added sodium methoxide (1 mol equiv. based on quantity of mono- and di-substitution product present) in methanol and, after stirring the reaction briefly, the methanol was removed under reduced pressure. The residue was extracted between ether and water, the aqueous layer re-extracted with ether and the combined ether layers dried and evaporated to yield a mixture of the starting mono- and disubstituted esters (ratio 1:3, respectively). After acidification of the aqueous layer above to pH 1, it was extracted twice with ether and the combined ether layers dried and evaporated to yield a mixture of acids of the starting esters (ratio mono- to di-substitution; 11:1). Approximately equal amounts of material were recovered from the original aqueous and ether layers in extraction of the residue above.

The mixture for the case of R = $MeC{\equiv}CCH_2$ (ratio mono: disubstitution 6:1) was separated as described above to give the dioic acid $MeC{\equiv}CCH_2CH(CO_2H)_2$ (35%) after recovery from the aqueous layer. The combined ether layers on evaporation gave a mixture of mono- and di-substituted esters (ratio 2.8:1). Repetition of this separation procedure using more sodium methoxide (1 mol equiv.) gave a further quantity (16%) of the same dioic acid (total 51%). Both the monosubstituted dioic acids above were used directly as described below.

Hydrolysis and Decarboxylation of Substituted Dimethyl Propanedioates.—Disubstituted propane-1,3-dioic acids were obtained by heating the above substituted propanedioates and sodium hydroxide (2M; 4 mol. equiv.) to boiling, adding sufficient ethanol to ensure a homogeneous solution and then heating under reflux for 4 h. After removal of the ethanol under reduced pressure, the residual solution was extracted with ether (the ether layer was then discarded) and the aqueous layer separated, cooled in ice and acidified to pH 1 by the dropwise addition of conc. hydrochloric acid. The mixture was extracted twice with ether and the ether layers combined, dried and evaporated to give the corresponding 1,3-dioic acids in 80—90% yields. 2,2-Di(prop-2-ynyl)propane-1,3-dioic acid[17] was obtained as colourless crystals, m.p. 125—137 °C (from 5M-hydrochloric acid); δ 8.92 (br s, CO_2H), 2.99 (d, *J* 3 Hz, CH_2), and 2.08 (t, *J* 3 Hz, C≡CH).

Decarboxylation of the crude disubstituted dioic acids, prepared as above, or the corresponding monosubstituted dioic acids, isolated by the separation procedure described earlier, was carried out by heating the acid in an oil-bath at 140—175 °C until gas evolution ceased (*ca.* 1 h). Distillation of the residue (Kugelrohr) gave the following acids in 76—90% yields: pent-4-ynoic acid (**12**), b.p. 90—110 °C/0.1 mmHg, solidified on standing (lit.,[18] m.p. 53—55 °C); δ 10.42 (br s, CO_2H), 2.53 (m, CH_2CH_2), and 1.96 (t, 3 Hz, C≡CH); hex-4-ynoic acid (**14**) b.p. 130—150 °C/0.1 mmHg, solidified with time (lit.,[19] m.p. 100—101 °C); δ 10.42 (br s, CO_2H), 2.47 (m, CH_2CH_2), and 1.72 (t, *J* 2

* It seems likely that, as in the case of (**32**) and (**26**), conformation of (**35**) for this ring fused azirine is preferred for a similar reason although difficulties in constructing a precise model in the case of (**35**) make this conclusion less secure.

Hz, Me); 2-(prop-2-ynyl)pent-4-ynoic acid (**13**) (not distilled); δ 10.91 (br s, CO_2H), 2.69 (m, 2 × CH_2, CH), and 2.02 (t, *J* 3 Hz, 2 × C≡CH); 2-(but-2-ynyl)hex-4-ynoic acid (**15**), b.p. 130—150 °C/1.5 mmHg, solidified on standing; δ 11.44 (br s, CO_2H), 2.53 (m, 2 × CH_2, CH), and 1.71 (t, *J* 2 Hz, 2 × Me); 2-(prop-2-ynyl)pent-4-enoic acid, b.p. 130—132 °C/19 mmHg; δ 11.02 (br s, CO_2H), 5.50 (m, CH=CH_2), 2.40 (m, 2 × CH_2, CH), and 2.02 (t, *J* 2.5 Hz, C≡CH).

Conversion of Pent-4-ynoic Acid (**12**) *to Hex-5-ynoic Acid* (**16**).—Pent-4-ynoic acid (12.8 g) in dry ether (81 ml) was added dropwise with stirring to a rapidly stirred solution of lithium aluminium hydride (10 g) in dry ether (300 ml). After the addition, the solution was heated under reflux for 2 h, cooled, and sufficient acetone was added to destroy excess hydride. Water was then added dropwise with vigorous stirring until the suspension changed from grey to white. The precipitated salts were separated, and the ether solution was dried and evaporated and the residual oil distilled to give pent-5-ynol, b.p. 78—82 °C/29 mmHg (9.3 g, 85%); δ3.67 (t, *J* 7 Hz, CH_2OH), 2.71 (br s, OH), 2.27 (td, *J* 7 and 2 Hz, CH_2C≡CH), 1.95 (t, *J* 2 Hz, C≡CH), and 1.74 (quint., *J* 7 Hz, $CH_2CH_2CH_2$). Pent-5-ynol was converted to its toluene-*p*-sulphonate[13] and the crude sulphonate (17.7 g) together with potassium cyanide (9.9 g) in dimethyl sulphoxide (200 ml) was heated in an oil-bath at 50—60 °C with stirring for 2 h, then for 2 days at room temperature. The mixture was poured into water and extracted three times with ether. The combined ether layers washed twice with water, dried, and the bulk of the ether was removed by distillation at atmospheric pressure keeping the temperature of the oil-bath at 45—50 °C. Hydrolysis of the residual oil, [pent-5-ynyl cyanide, δ 2.48 (t, *J* 7 Hz, CH_2CN), 2.31 (td, *J* 7 and 2 Hz, CH_2C≡CH), 2.01 (t, *J* 2 Hz, C≡CH), and 1.84 (quint., *J* 7 Hz, $CH_2CH_2CH_2$); $\nu_{max.}$ 2 260 and 2 160 cm^{-1}] was carried out using aqueous potassium hydroxide [43 g in water (125 ml)] and methanol (100 ml) by heating under reflux overnight. The solution was worked up as described earlier for disubstituted propane-1,3-dioic acids. Hex-5-ynoic acid (**16**) was obtained as an oil (lit.,[18] m.p. 41—43.5 °C); δ 8.30 (br s, CO_2H), 2.48 (t, *J* 8 Hz, CH_2CO_2H), 2.26 (td, *J* 8 and 3 Hz, CH_2C≡CH), 1.96 (t, *J* 3 Hz, C≡CH), and 1.83 (quint., *J* 8 Hz, $CH_2CH_2CH_2$); $\nu_{max.}$ 2 120 and 1 700 cm^{-1}. This was used directly as described below.

Methyl N-*Substituted Anthranilates*.—These derivatives of the above carboxylic acids were obtained in 77—81% yields by successive treatment with thionyl chloride and methyl anthranilate as described previously.[2] The following compounds were obtained in this way: methyl *N*-(pent-4-ynoyl)anthranilate as colourless crystals, m.p. 48—51 °C (from ethanol); δ 11.04 (br s, NH), 8.65 (dd, *J* 8 and 1 Hz, 3-H), 7.96 (dd, *J* 8 and 2 Hz, 6-H), 7.49 (ddd, *J* 8, 8 and 2 Hz, 4-H), 7.02 (ddd, *J* 8, 8, and 1 Hz, 5-H), 3.86 (s, OMe), 2.62 (m, 2 × CH_2), and 1.95 (t, *J* 2 Hz, C≡CH); methyl *N*-(hex-4-ynoyl)anthranilate as an oil; δ 10.93 (br s, NH), 8.68 (dd, *J* 8 and 1 Hz, 3-H), 7.94 (dd, *J* 8 and 2 Hz, 6-H), 7.48 (ddd, *J* 8, 8, and 2 Hz, 4-H), 7.02 (ddd, *J* 8, 8, and 1 Hz, 5-H), 3.86 (s, OMe), 2.56 (m, 2 × CH_2), and 1.72 (t, *J* 2 Hz, C≡CMe); methyl *N*-(hex-5-ynoyl)anthranilate as an oil; δ 11.3 (br s, NH), 8.9 (dd, *J* 8 and 1 Hz, 3-H), 8.15 (dd, *J* 8 and 2 Hz, 6-H), 7.65 (ddd, *J* 8, 8, and 2 Hz, 4-H), 7.15 (ddd, *J* 8, 8, and 1 Hz, 5-H), 3.96 (s, OMe), and 2.75—1.90 (m, $CH_2CH_2CH_2$, C≡CH); *methyl* N-(*hepta*-1,6-*diyn*-4-*oyl*)*anthranilate* as colourless crystals, m.p. 90.5—92 °C (from ethanol) (Found: C, 71.2; H, 5.6. N, 5.2. $C_{16}H_{15}NO_3$ requires C, 71.4; H, 5.6; N, 5.2%); δ 11.18 (br s, NH), 8.66 (dd, *J* 8 and 1 Hz, 3-H), 7.97 (dd, *J* 8 and 2 Hz, 6-H), 7.48 (ddd, *J* 8, 8, and 2 Hz, 4-H), 7.03 (ddd, *J* 8, 8, and 1 Hz, 5-H), 3.88 (s, OMe), 2.64 (m, 2 × CH_2, CH), and 1.99 (t, *J* 2 Hz, 2 × C≡CH); methyl *N*-(nona- 2,7-diyn-5-oyl)anthranilate as colourless crystals, m.p. 65—68 °C (from ethanol), δ 11.11 (br s, NH), 8.70 (dd, *J* 8 and 1 Hz, 3-H), 7.96 (dd, *J* 8 and 2 Hz, 6-H), 7.48 (ddd, *J* 8, 8, and 2 Hz, 4-H), 7.03 (ddd, *J* 8, 8, and 1 Hz, 5-H), 3.88 (s, OMe), 2.64 (m, 2 × CH_2, CH), and 1.7 (m, 2 × C≡CMe); methyl *N*-(hept-6-en-1-yn-4-oyl)anthranilate as an oil; δ (60 MHz) 11.02 (br s, NH), 8.76 (d, *J* 8 Hz, 3-H), 7.96 (d, *J* 8 Hz, 6-H), 7.51 (dd, *J* 8 and 8 Hz, 4-H), 7.01 (dd, *J* 8 and 8 Hz, 5-H), 5.66 (m, C*H*=CH_2), 5.08 (m, CH=CH_2), 3.91 (s, OMe), 2.56 (m, 2 × CH_2), and 2.00 (m, C≡CH).

3-*Amino*-2-*substituted Quinazolones*.—The above amides in which the acid part was unbranched, were heated with hydrazine hydrate (96%) in methanol or ethanol as previously described[2] and the following compounds were obtained as colourless crystals: 3-*amino*-2-(*but*-1-*yn*-4-*yl*)*quinazolin*-4(3H)-*one* (**7**) (46%), m.p. 157—159.5 °C (from methanol) (Found: C, 67.5; H, 5.3; N, 19.7. $C_{12}H_{11}N_3O$ requires C, 67.6; H, 5.2; N, 19.7); δ 8.18 (d, *J* 8 Hz, 5-H), 7.63—7.29 (m, 6-, 7-, and 8-H), 4.88 (br s, NH_2), 3.28 (t, *J* 7 Hz, CH_2CH_2C≡), 2.75 (td, *J* 7 and 2 Hz, CH_2C≡CH), and 1.96 (t, *J* 2 Hz, C≡CH); $\nu_{max.}$ 3 290m, 3 230m, 1 665s, 1 620s, 770s, and 690s cm^{-1}; 3-*amino*-2-(*pent*-3-*yn*-1-*yl*)*quinazolin*-4(3H)-*one* (**9**) (90%), m.p. 147—150 °C (from ethanol) (Found: C, 68.7; H, 5.8; N, 18.5. $C_{13}H_{13}N_3O$ requires C, 68.7; H, 5.8; N, 18.5%); δ 8.15 (d, *J* 8 Hz, 5-H), 7.60—7.26 (m, 6-, 7-, and 8-H), 4.94 (br s, NH_2), 3.20 (t, *J* 7 Hz, CH_2CH_2C≡), 2.70 (m, CH_2C≡CMe), and 1.70 (t, *J* 2 Hz, C≡CMe); $\nu_{max.}$ 3 300m, 3 205w, 1 640s, 1 595s, 760m, and 690s cm^{-1}; 3-*amino*-2-(*pent*-5-*yn*-1-*yl*)*quinazolin*-4(3H)-*one* (**11**) (70%) m.p. 106—107 °C (from ethanol) (Found: C, 68.5; H, 5.9; N, 18.5; $C_{13}H_{13}N_3O$ required C, 68.7; H, 5.8; N, 18.5%); δ 8.15 (d, *J* 8 Hz, 5-H), 7.6—7.1 (m, 6-, 7-, and 8-H), 4.84 (br s, NH_2), 3.10 (t, *J* 7 Hz, CH_2(CH_2)$_2$C≡), 2.35 (td, *J* 7 and 2 Hz, CH_2CH_2C≡), 2.05 (quint. *J* 7 Hz, CH_2C≡), and 1.96 (t, *J* 2 Hz, C≡CH); $\nu_{max.}$ 3 315m, 3 240m, 1 672s, 1 596s, 781m, and 696 cm^{-1}. The methyl *N*-substituted anthranilates above in which the acid part contained a branched chain were heated with hydrazine hydrate (96%) in methanol or ethanol in a sealed tube in the absence of oxygen as described previously[1] and the following compounds were obtained as colourless crystals: 3-*amino*-2-(*hepta*-1,6-*diyn*-4-*yl*)*quinazolin*-4(3H)-*one* (**8**) (63%), m.p. 124—125.5 °C (from ethanol) (Found: C, 71.6; H, 5.3; N, 16.7. $C_{15}H_{13}N_3O$ requires C, 71.7; H, 5.2; N, 16.7%); δ 8.20 (d, *J* 8 Hz, 5-H), 7.64—7.31 (m, 6-, 7-, and 8-H), 4.96 (br s, NH_2), 4.20 (quint., *J* 7 Hz, CH), 2.76 (dd, *J* 7 and 2 Hz, 2 × CH_2), and 1.92 (t, *J* 2 Hz, 2 × C≡CH); 3-*amino*-2-(*nona*-2,7-*diyn*-5-*yl*)*quinazolin*-4(3H)-*one* (**10**) (59%), m.p. 104—105 °C (from ethanol) (Found: C, 72.8; H, 6.2; N, 15.0. $C_{17}H_{17}N_3O$ requires C, 73.1; H, 6.1; N, 15.0%); δ 8.22 (d, *J* 8 Hz, 5-H), 7.72—7.30 (m, 6-, 7-, and 8-H), 5.10 (br s, NH_2), 4.09 (quint., *J* 7 Hz, CH), 2.67 (m, 2 × CH_2), and 1.69 (t, *J* 2 Hz, 2 × C≡CMe); $\nu_{max.}$ 3 310m, 1 680s, 1 600s, 1 583s, 768s, and 691s cm^{-1}; 3-*amino*-2-(*hept*-1-*en*-6-*yn*-4-*yl*)*quinazolin*-4(3H)-*one* (**38**) (53%), m.p. 60—62 °C (from ethanol) (Found: C, 71.1; H, 5.9; N, 16.5. $C_{15}H_{15}N_3O$ requires C, 71.1; H, 6.0; N, 16.6%); δ 8.18 (d, *J* 8 Hz, 5-H), 7.63—7.29 (m, 6-, 7-, and 8-H), 5.73 (m, C*H*=CH_2), 5.07 (m, CH=CH_2), 4.89 (br s, NH_2), 4.06 (quint., *J* 7 Hz, CH), 2.65 (dd, *J* 7 and 2 Hz, CH_2C≡CH), 2.57 (m, CH_2CH=CH_2), and 1.88 (t, *J* 2 Hz, C≡CH); $\nu_{max.}$ 3 320m, 3 260s, 1 660s, 1 590s, 925m, 780s, and 700s cm^{-1}.

Oxidation of 2-*Substituted* 3-*Aminoquinazolin*-(3H)-4-*ones* (**7**)—(**11**) *with Lead Tetra-acetate under Conditions of High Dilution*.—In these experiments all glassware was flame-dried under a current of dry nitrogen immediately prior to use. The foregoing aminoquinazolones (100 mg or 200 mg, 1 mol equiv.) was dissolved in dry dichloromethane (50 ml) and lead tetra-acetate (1.15 mol equiv.) was also dissolved in an equal volume of dry dichloromethane. Both solutions were added simultaneously at the same rate over 20—40 min. to rapidly stirred dry dichloromethane (100 ml) which was cooled in an ice bath.

After the reaction had been stirred for a further 10—30 min the precipitated lead diacetate was separated and the solution washed with aqueous sodium hydrogen carbonate, dried, and evaporated to give the product. Oxidation of compound (**9**) in this way gave a solid product in quantitative yield. Crystallisation from ethyl acetate–light petroleum gave the *azirine* (**17**) as colourless prisms (78%), m.p. 135—136 °C (Found: C, 69.2; H, 5.0; N, 18.6. $C_{13}H_{11}N_3O$ requires C, 69.3; H, 4.9; N, 18.7%) δ_H (400 MHz) 8.05 (ddd, *J* 8, 1.5, and 0.5 Hz, 6-H), 7.64 (ddd, *J* 8, 7, and 1.5 Hz, 8-H), 7.56 (ddd, *J* 8, 1.5, and 0.5 Hz, 9-H), 7.34 (ddd, *J* 8, 7, and 1.5 Hz, 7-H), 3.48 (ddd, *J* 17.5, 10.9, and 9.3 Hz, 1-H), 3.03 (ddd, *J* 17.5, 9.7, and 1.5 Hz, 1-H), 2.71 (s, Me), 2.61 (ddd, *J* 13.9, 10.9, and 9.7 Hz, 2-H), and 1.73 (ddd, *J* 13.9, 9.3, and 1.5 Hz, 2-H); δ_C (100 MHz) 171.50 (s), 160.80 (s), 158.48 (s), 148.70 (s), 134.30 (d), 126.92 (d), 126.34 (d), 126.16 (d), 120.92 (s), 55.91 (s), 29.42 (dd), 28.15 (dd), and 14.96 (q); $\nu_{max.}$ 1 780w, 1 675s, 1 630s, 1 610s, 780s, and 700m cm^{-1}.

The oxidation of compound (**10**) (1 g) as described above gave a solid (950 mg) whose n.m.r. spectrum indicated it was pure. Crystallisation from ethanol gave *azirine* (**23**) as colourless needles, m.p. 140.5—141.5 °C (Found: C, 73.7; H, 5.5; N, 15.2. $C_{17}H_{15}N_3O$ requires C, 73.6; H, 5.5; N, 15.2%); δ (400 MHz) 8.14 (ddd, *J* 8, 1.5, and 0.6 Hz, 6-H), 7.72 (ddd, *J* 8.2, 6.5, and 1.5 Hz, 8-H), 7.68 (ddd, *J* 8.2, 1.7, and 0.6 Hz, 9-H), 7.42 (ddd, *J* 8, 6.5, and 1.7 Hz, 7-H), 3.79 (dddd, *J* 10.5, 8.3, 7.4, and 4.4 Hz, 1-H), 2.94 (ddq, *J* 16.8, 4.4, and 2.5 Hz, C*H*HC≡CMe), 2.79 (s, azirine Me), 2.76 (ddq, *J* 16.8, 7.4, and 2.5 Hz, CH*H*C≡CMe), 2.65 (dd, *J* 13.7 and 10.5 Hz, 2-H), 1.97 (dd, *J* 13.7 and 8.3 Hz, 2-H), and 1.74 (t, *J* 2.5 Hz, MeC≡C); $\nu_{max.}$ 1 760w, 1 690s, 1 628m, 1 610m, 1 330m, and 780s cm^{-1}.

The oxidation of compound (**7**) as described above and examination of the crude product by n.m.r. showed the presence of the azirine (**20**) and the acetic acid addition product (**21**) in the ratio 79:21, respectively. The azirine (**20**) showed δ (400 MHz) 10.41 (dd, *J* 2.8 and 0.6 Hz, azirine CH), 8.02 (dd, *J* 8 and 1.5 Hz, 6-H), 7.63 (ddd, *J* 8.1, 6.9 and 1.5 Hz, 8-H), 7.54 (dd, *J* 8.1 and 1.7 Hz, 9-H), 7.32 (ddd, *J* 8, 6.9, and 1.7 Hz, 7-H), 3.47 (ddd, *J* 17.5, 10.9, and 9.3 Hz, 1-H), 3.03 (ddd, *J* 17.5, 9.6, and 1.3 Hz, 1-H), 2.65 (dddd, *J* 13.9, 10.9, 9.6, and 2.8 Hz, 2-H), and 1.75 (dddd, *J* 13.9, 9.3, 1.3, and 0.6 Hz, 2-H). When the above reaction mixture was set aside overnight before work-up, an n.m.r. spectrum of the crude product showed the presence of the aziridine (**21**) only, which was isolated as an unstable (non-distillable) oil; δ 8.00 (d, *J* 8 Hz, 6-H), 7.68—7.24 (m, 7-, 8-, and 9-H), 6.10 (d, *J* 8 Hz, C*H*OAc), 3.88 [br d, *J* 8 Hz, (exch. D_2O), NH], 3.08 (t, *J* 9 Hz 1-H_2), 2.31 (t, *J* 9 Hz, 2-H_2), and 2.09 (s, OCOMe). On shaking with D_2O, δ 6.10 (d) collapsed to δ 6.10 (s).

The oxidation of compound (**8**) was carried out as described above but the reaction was worked up 10 min after the reagents had been mixed together and this gave only the azirine (**22**), m.p. 163—168 °C as a colourless solid (from ether–dichloromethane). A satisfactory analysis of this material was not obtained; δ (400 MHz) 10.48 (dd, *J* 2.8 and 0.6 Hz, azirine CH), 8.13 (dd, *J* 8 and 1.4 Hz, 6-H), 7.73 (ddd, *J* 8.2, 6.8, and 1.4 Hz, 8-H), 7.69 (dd, *J* 8.2 and 1.3 Hz, 9-H), 7.43 (ddd, *J* 8, 6.8, and 1.3 Hz, 7-H), 3.88 (dddd, *J* 10.6, 8.1, 7.3 and 4.4 Hz, 1-H), 2.99 (ddd, *J* 17, 4.4, and 2.6 Hz, H*H*CC≡CH), 2.86 (ddd, *J* 17, 7.3, and 2.6 Hz, *H*HCC≡CH), 2.75 (ddd, *J* 13.7, 10.6, and 2.8 Hz, 2-H), 2.04 (dd, *J* 13.7 and 8.1 Hz, 2-H), and 1.99 (t, *J* 2.6 Hz, C≡CH). When the above reaction mixture was set aside overnight prior to work-up, an n.m.r. spectrum of the crude product showed the presence of the acetic acid addition product (**24**) only. Crystallisation from ether–dichloromethane gave the *aziridine* (**24**), m.p. 128—131 °C (decomp.) (Found: C, 66.1; H, 5.0; N, 13.6. $C_{17}H_{15}N_3O_3$ requires C, 66.0; H, 4.9; N, 13.6%); δ (400 MHz) 8.18 (ddd, *J* 8, 1.5, and 0.5 Hz, 6-H), 7.75 (ddd, *J* 8.2, 7, and 1.5 Hz, 8-H), 7.66 (ddd, *J* 8.2, 1.1, and 0.5 Hz, 9-H), 7.46 (ddd, *J* 8, 7, and 1.1 Hz, 7-H), 6.35 (d, *J* 8.5 Hz, C*H*OAc), 3.69 (br d, *J* 8.5 Hz, NH), 3.54 (dddd, *J* 9.4, 7.9, 5.5, and 4.4 Hz, 1-H), 2.85 (ddd, *J* 16.9, 4.4, and 2.6 Hz, H*H*CC≡CH), 2.75 (ddd, *J* 16.9, 7.9, and 2.6 Hz, *H*HCC≡CH), 2.57 (dd, *J* 14.3 and 9.4 Hz, 2-H), 2.45 (dd, *J* 14.3 and 5.5 Hz, 2-H), 2.16 (s, OCOMe), and 1.98 (t, *J* 2.6 Hz, C≡CH); $\nu_{max.}$ 3 230br s, 1 745s, 1 670s, 1 615s, 1 225s, 1 140s, 995m, 775s, and 695m cm^{-1}.

The oxidation of compound (**11**) (1 g) as described above and examination of the crude reaction product by n.m.r. showed the presence of the azirines (**30**) and (**31**) in a 9:4 ratio, respectively. Crystallisation from methanol gave a pure sample of the azirine (**30**) (250 mg), m.p. 120—124 °C, but an analytical sample could not be obtained since the (colourless) azirine produced an orange polymeric substance when allowed to stand overnight; δ (400 MHz) 10.28 (d, *J* 2.3 Hz), 8.14 (dd, *J* 7.9 and 1.5 Hz, 7-H), 7.73 (ddd, *J* 8.1, 7.1, and 1.5 Hz, 9-H), 7.62 (dd, *J* 8.1 and 1.3 Hz, 10-H), 7.42 (ddd, *J* 7.9, 7.1, and 1.3 Hz, 8-H), 3.39 (ddd, *J* 15.4, 11.9, and 5.9 Hz, 1-H), 3.05 (ddd, *J* 15.4, 5.6, and 5.1 Hz, 1-H), 2.62 (dddd, *J* 14.9, 8.9, 4.6, and 2.3 Hz, 3-H), 2.38 (ddddd, *J* 13.6, 8.9, 5.9, 5.1, and 4.6 Hz, 2-H), 1.97 (ddddd, *J* 13.6, 11.9, 8.9, 7.2, and 5.6 Hz, 2-H), and 1.51 (ddd, *J* 14.9, 8.9, and 7.2 Hz, 3-H); $\nu_{max.}$ 1 668s, 1 610s, 790m, and 720m cm^{-1}. The n.m.r. spectrum of the azirine (**31**) was obtained from that of the crude reaction product above by subtraction of those signals belonging to azirine (**30**) and showed δ (400 MHz) 8.29 (dd, *J* 7.9 and 1.5 Hz, 9-H), 7.71 (ddd, *J* 8.1, 7.1, and 1.5 Hz, 7-H), 7.56 (dd, *J* 8.1 and 1.3 Hz, 6-H), 7.46 (ddd, *J* 7.9, 7.1, and 1.3 Hz, 10-H), 4.42 (s, 11a-H), 3.32 (ddd, *J* 13, 5, and 1.5 Hz, 2-H), 3.28 (ddd, *J* 15, 7.7, and 1.5 Hz, 4-H), 3.11 (ddd, *J* 15, 12.3, and 1.5 Hz, 4-H), 2.99 (ddd, *J* 13, 12.7, and 7.7 Hz, 2-H), 2.55 (ddddd, *J* 13.5, 7.7, 7.7, 1.5 and 1.5 Hz, 3-H), and 1.65 (ddddd, *J* 13.5, 12.7, 12.3, 5, and 1.5 Hz, 3-H).

Attempted Trapping of a 1H-*Azirine Intermediate*.—The *N*-aminoquinazolin-4(3*H*)-*one* (**7**) (200 mg, 1 mol equiv.) was dissolved in dry dichloromethane (50 ml) and lead tetra-acetate (0.9 mol equiv.) was also dissolved in an equal volume of dry dichloromethane. Both solutions were added simultaneously at the same rate over 20 min to rapidly stirred dry dichloromethane (100 ml) which was cooled in a solid CO_2–acetone bath at −78 °C. After the addition was complete, the solution was stirred for a further 8 h. No precipitated lead diacetate was visible in the solution after this time, however, and testing with starch-iodide paper suggested that unchanged LTA was still present. 2,3-Dimethylbutadiene (1.3 g, 16 mol equiv.) was then added to the reaction mixture and the temperature of the solution allowed to rise slowly to ambient, with stirring throughout. The solution was washed twice with aqueous sodium hydrogen carbonate, dried, and evaporated. An n.m.r. spectrum of the crude reaction mixture showed the presence of the acetoxyaziridine (**21**) and aziridine (**29**) in a ratio of 3:2, respectively. Rapid chromatography on alumina and elution with light petroleum–ethyl acetate (4:1) gave the *aziridine* (**29**) (18 mg) as colourless laths, m.p. 96—97 °C (from ethanol) (Found: C, 73.7; H, 6.5; N, 14.4. $C_{18}H_{19}N_3O$ requires C, 73.7; H, 6.5; N, 14.3%); δ (400 MHz) 8.11 (dd, *J* 8 and 1.5 Hz, 5-H), 7.63 (ddd, *J* 8.2, 6.9, and 1.5 Hz, 7-H), 7.57 (dd, *J* 8.2 and 1.4 Hz, 8-H), 7.36 (ddd, *J* 8, 6.9, and 1.4 Hz, 6-H), 5.16 (br s, =C*H*H), 5.10 (m, =CH*H*), 3.13 (ddd, *J* 16.2, 8.3, and 6.4 Hz, 1″-H), 3.02 (m, 2, 3′-H_2), 2.90 (ddd, *J* 16.2, 7.9, and 7.9 Hz, 1″-H), 2.71 (m, CH_2C≡CH), 1.89 (t, *J* 2.6 Hz, C≡CH), 1.76 (br s, =CMe), and 1.22 (s, aziridine Me). Minor invertomer, 1.59 (s, aziridine Me), and 1.43 (s, =CMe). The ratio of the two invertomers was *ca.* 17:1; $\nu_{max.}$ (Nujol) 3 250m, 1 660s, 1 590s, 1 300w, 1 120w, 900m, and 780m cm^{-1}.

The oxidation of compound (**7**) (0.3 g) with LTA (0.65 g, 1.15 mol equiv.) in dichloromethane (5 ml) and 2,3-dimethylbutadiene (5 ml) at 0 °C in the usual way gave the aziridine (**29**)

only. Rapid chromatography on alumina and elution with light petroleum–ethyl acetate (3:1) gave the pure aziridine (51%).

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