Aziridination of Alkenes using 3-Amino-2-ethylquinazolin-4(3*H*)-one and Lead Tetra-acetate–Trifluoroacetic Acid

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Efficient aziridination of terminal alkenes by oxidative addition [lead tetra-acetate (LTA)] of the *N*-aminoquinazoline (**1**) is effected by inclusion of trifluoroacetic acid (TFA) in the mixture. The effect of (a) substitution of either lead tetratrifluoroacetate or [bis(trifluoroacetoxy)iodo]benzene for LTA or (b) addition of preformed *N*-acetoxyaminoquinazolone (**7**) to allyl chloride in the presence of TFA, suggests that the major factor in bringing about improved aziridination yields of allyl chloride and other unreactive alkenes is protonation of the quinazolone ring.

The title *N*-aminoquinazolone (**1**) is one member of a family of *N*-aminoheterocyclic compounds whose oxidation with lead tetra-acetate (LTA) in the presence of alkenes gives aziridines.[1] Recent work has identified (**2**) as the aziridinating agent from the oxidation of the quinazolone (**1**): (**2**) appears to be playing the role previously assigned to the *N*-nitrene (**3**).[2]

Aziridinations using the oxidative addition of (**1**) (and other members of the family referred to above) to many electron-rich or electron-deficient alkenes proceed in good yields. Thus both styrene and methyl acrylate react with (**2**) to give the corresponding aziridines (**4**) and (**5**) in 75 and 80% yields, respectively, using only 1.5 mol equiv. of the alkenes. The mechanism by which (**2**) brings about aziridination of alkenes may resemble that by which peracids bring about epoxidation of alkenes (the Bartlett mechanism) (Figure 1).[3,4]

The reactivity of alkenes towards peracids diminishes as the number of alkyl substituents on the double bond is reduced. Likewise, the least reactive double bonds towards aziridination by oxidative addition of (**1**) and related *N*-aminoheterocyclic compounds are (monosubstituted) terminal alkenes, from which the yields of aziridine are little better than 10%.[5]

Since the yields for the epoxidation of terminal alkenes are improved by using (buffered) trifluoroperacetic acid[6] instead of peracetic acid, it was of interest to apply the same tactic to the case of aziridination.

We had previously observed that the presence of trifluoroacetic acid (TFA) in the oxidative addition of (**6**) to α,β-unsaturated esters and α,β-unsaturated ketones had a remarkable effect on the reactivity, and particularly on the facial reactivity, of prochiral double bonds in these alkenes.[7] Since the reactive intermediate in the oxidative addition of (**6**) to alkenes in the *absence* of TFA was subsequently shown to be the acetoxyaminoquinazolone (**7**)[8] [*cf.* (**2**) above], it was conceivable that the greater reactivity in the *presence* of TFA could be ascribed to the trifluoroacetoxyaminoquinazolone (**8**), where exchange of the acetate ligands on the lead by trifluoroacetate and subsequent transfer of the trifluoroacetoxy group to the amino group of (**6**) takes place in the oxidation. Alternatively, TFA could bring about the exchange of the acetoxy group in (**7**) by trifluoroacetoxy.

Oxidation of a number of terminal alkenes was therefore examined using (**1**) in the presence of TFA, with the assumption that formation of the (protonated) trifluoroacetoxyaminoquinazolone (**9**) takes place *in situ*.

Oxidation of the *N*-aminoquinazolone (**1**) in the presence of allyl chloride (1.5 mol equiv.) gives less than 10% of the aziridine (**10**) from examination of the crude reaction product. Even when the oxidation is carried out in neat allyl chloride, the isolated

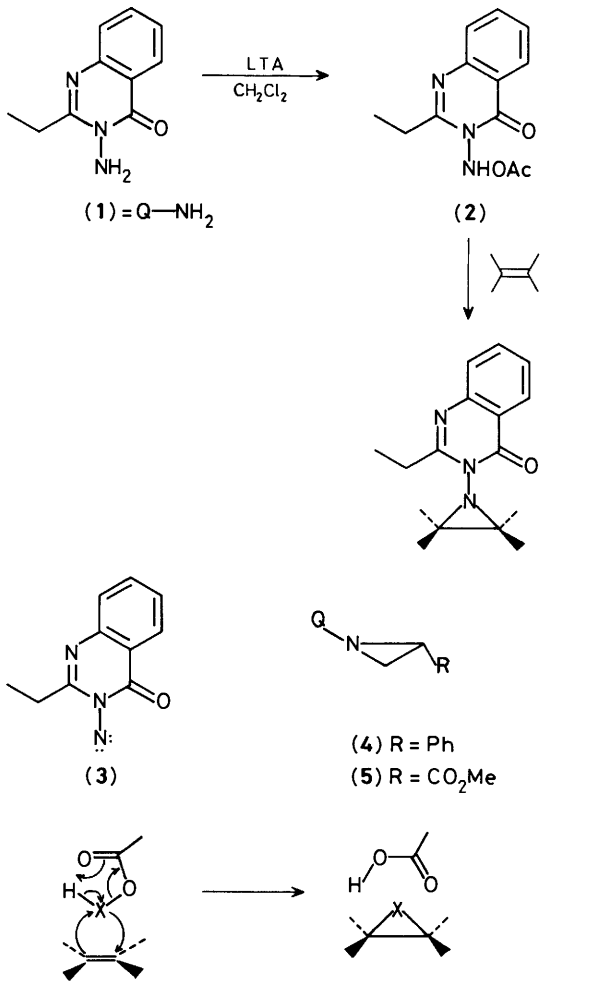
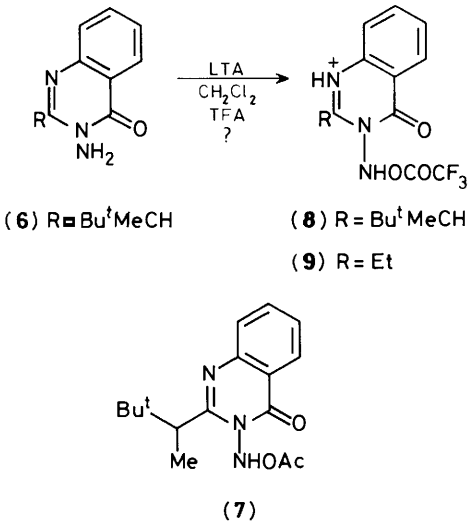


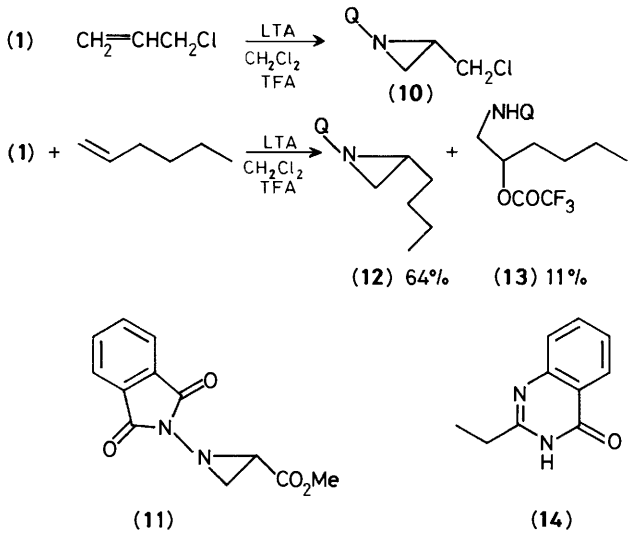
Figure 1. Epoxidation, X = O; aziridination, X = NQ

yield of aziridine (**10**) is only 20%. The same reaction carried out in the presence of allyl chloride (1.5 mol equiv.) and TFA (3 mol equiv.) gave an 85% isolated yield of (**10**), m.p. 87—89 °C.[9] The structure of (**10**) follows unambiguously from its n.m.r. spectrum in which the protons within each of the chloromethyl and ethyl methylene groups are diastereotopic.

It is noteworthy that the aziridine (**10**) survives the strongly acidic conditions of the reaction, presumably as a result of preferential protonation of the quinazolone ring and of the



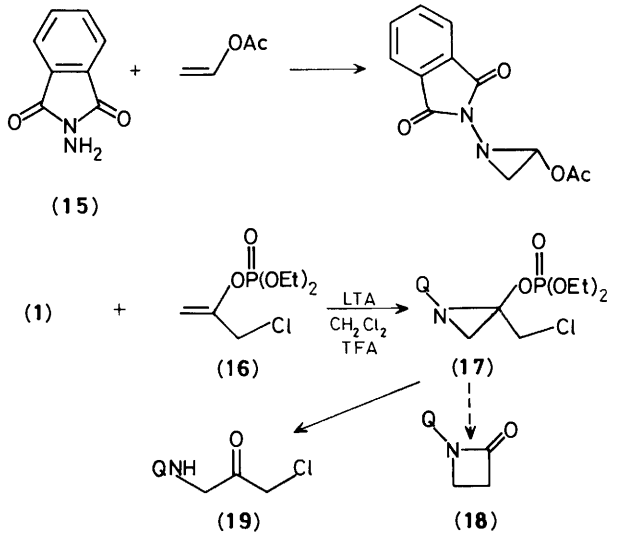
electron-withdrawing effect of the chloromethyl group (see below). We have shown elsewhere that the aziridine (**11**) bearing the less basic *N*-phthalimido substituent is rapidly ring-opened by TFA.[10] Similarly, in epoxidation using trifluoroperacetic acid, it is essential to buffer the solution to avoid ring-opening of the epoxide.[6]



Oxidation of the *N*-aminoquinazolone (**1**) in the presence of hex-1-ene gave the aziridine (**12**) in 11% yield; the presence of TFA (3 mol equiv.) in the reaction mixture increased the yield to 64%. In addition, the unstable ring-opened trifluoroacetate (**13**) (11%) was also isolated: clearly the aziridine (**12**) is less stable than (**10**) towards attack by TFA.

The effect of lowering the TFA concentration in this experiment was investigated: using only 1.8 mol equiv. of TFA, the isolated yields of (**12**) and (**13**) were reduced to 37 and 5% respectively, with 27% of the deaminated quinazolone (**14**) also being obtained. The latter is the major isolated product (80%) when oxidation of the quinazolone (**1**) is carried out in the presence of unreactive alkenes or in the absence of alkene.

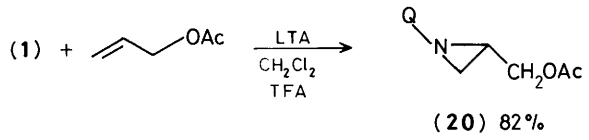
Since vinyl acetate is aziridinated in good yield by oxidative addition of *N*-aminophthalimide (**15**),[11] aziridination of the diethoxyphosphoryl substituted allyl chloride (**16**)[12] had previously been attempted: it was our intention to find conditions which would induce rearrangement of the product aziridine (**17**) to the β-lactam (**18**) (Scheme 1).



Scheme 1.

Unexpectedly, however, no aziridine (**17**) was formed under these conditions, and only the deaminated quinazolone (**14**) was isolated (68%). Repetition of the reaction in the presence of TFA (6 mol quiv.) does, presumably, bring about aziridination of (**16**), but the isolated product is the chloroketone (**19**) (71%), m.p. 117—118 °C, formed by ring-opening of the (protonated) aziridine (**17**) with loss of the phosphoryl group.

Allyl acetate is a further example of an alkene which can be aziridinated to give (**20**) in good yield (82%) by oxidation of (**1**) only in the presence of TFA (Scheme 2).



Scheme 2.

Investigation into the Mechanism of Aziridination in the Presence of TFA.—Oxidation of the *N*-aminoquinazolone (**1**) by slow addition of LTA at −20 °C gives an almost quantitative yield of the acetoxyaminoquinazolone (**2**). The successful aziridination of allyl chloride described above could also be accomplished in 80% yield by dropwise addition of a solution of (**2**), held at −20 °C, to a dichloromethane solution of the alkene (3 mol equiv.) containing TFA (6 mol equiv.) at 0 °C, and then allowing the solution to warm to ambient temperature.*

In view of the analogies between epoxidation using peracids and aziridination using (**2**) referred to earlier, it was surprising to find that we were incorrect in assuming that the exchange of the acetoxy for a trifluoroacetoxy group in (**2**) is necessary for the efficient aziridination of terminal alkenes. Thus oxidation of the *N*-aminoquinazolone (**1**) in deuteriochloroform at −20 °C, followed by separation of lead diacetate at −40 °C and n.m.r. examination of the deuteriochloroform solution after addition of TFA (*ca.* 3 mol equiv.) at −40 °C without any intermediate warming of the solution, showed downfield shifts for the resonances of the quinazolone ring protons and for the (still non-equivalent) methylene protons of the ethyl group. However, the chemical shift of the amine proton was hardly

* When this experiment was carried out by addition of TFA (3 mol equiv.) to a solution of (**2**) containing allyl chloride (2 mol equiv.), the aziridine (**10**) was isolated in only 43% yield after chromatography.

affected and two acetate group methyl signals of approximately equal intensity were visible, presumably corresponding to free acetic acid and the bound acetoxy group. Thus neither the NH nor the acetoxy group appear to be rapidly exchanging or exchanged. Slow decomposition of the acetoxyaminoquinazolone (**2**) occurs in the presence of TFA, and the deaminated quinazolone (**14**) is one of the products.

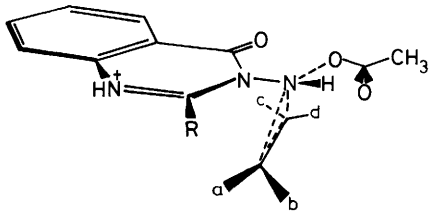
Conceivably, the aziridination could still have proceeded *via* the trifluoroacetoxyaminoquinazolone (**9**) in (undetected) equilibrium with the acetoxyaminoquinazolone (**2**) in the presence of TFA. However, oxidation of the *N*-aminoquinazolone (**1**) with lead tetratrifluoroacetate (LTTFA)[13] in the presence of allyl chloride gave (impure) aziridine (**10**) in only 28% yield. Likewise, oxidation of (**1**) with [bis(trifluoroacetoxy)iodo]benzene [$PhI(OCOCF_3)_2$] in the presence of allyl chloride gave the aziridine (**10**) in only 12% yield. Significantly, when the latter reaction was carried out in the presence of 1 mol equiv. of TFA the yield was raised to 78%, and in the presence of 2 mol equiv. of TFA a 94% yield of (**10**) was obtained. {Oxidations of (**1**) with LTA and with [bis(acetoxy)iodo]-benzene [$PhI(OAc)_2$] appear to proceed *via* the same intermediate acetoxyaminoquinazolone (**2**)* and it is therefore reasonable to assume that aziridinations using $PhI(OCOCF_3)_2$ will proceed *via* the corresponding trifluoroacetoxyaminoquinazolone (**9**)}.

It appears, therefore that the greatly increased reactivity in the oxidative addition of *N*-aminoquinazolone (**1**) to allyl chloride, and presumably also to other alkenes mentioned above, in the presence of TFA is largely due to protonation of the quinazolone ring and not just the result of exchange of acetoxy by trifluoroacetoxy in the reactive intermediate (**2**) if, in fact, this occurs.†

Support for this conclusion comes from the oxidation of *N*-aminophthalimide (**15**) in the presence of allyl chloride or hex-1-ene with either LTA in the presence of TFA [as for (**1**)] or [bis(trifluoroacetoxy)iodo]benzene: in both cases the only isolated product was phthalimide (50—60%). Clearly *N*-aminophthalimide lacks the basic site which at present in the quinazolone ring, protonation of which appears to be important in the aziridination of some otherwise unreactive alkenes.

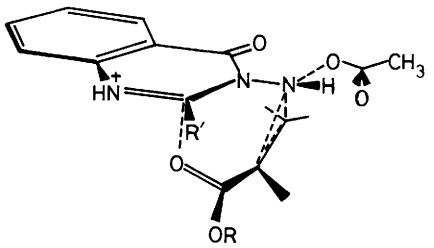
How does protonation of the quinazolone ring in (**2**) bring about increased efficiency in the aziridination of, *e.g.*, allyl chloride? We suggest that protonation of the quinazolone ring at N-1 (or on the carbonyl oxygen) facilitates the reaction by reducing the barrier to rotation around the N–N bond and thus lowering the energy of the transition state for aziridination, which resembles (**21**). In this transition state (**21**), eclipsing of the nitrogen lone pairs is required and will be reduced by delocalisation of the N-3 lone pair either *via* the amidine unit (protonation on N-1) or *via* the amide (protonation on the carbonyl oxygen).

At present, it is not clear which site on the alkene is occupied by the chloromethyl group in the addition to allyl chloride. An attractive *syn*-interaction between the carbonyl oxygen of α,β-unsaturated esters or α,β-unsaturated ketones and C-2 of the quinazolone ring (Figure 2) was proposed to account for the facial selectivity obtained in aziridination using (**6**) in the presence of TFA.[7b]‡ A transition state resembling that in Figure 2, with the chloromethyl group replacing the carbonyl group, would be expected to lead to a significantly higher level of asymmetric induction when R is chiral than one in which the chloromethyl group is located at any other position on the alkene.§ This point is under investigation.



(**21**)

a,b,c, or d = H,H,H, or CH_2Cl



R' = Bu^tMeCH

Figure 2.

Experimental

For general experimental details see ref. 15. N.m.r. spectra were measured at 300 MHz in $CDCl_3$ solution unless otherwise indicated.

Oxidation of N-*Aminoquinazolinone* (**1**) *with Lead Tetraacetate in the Presence of Alkenes and Trifluoroacetic Acid.*—The procedure described in ref. 7*b* was followed using the *N*-aminoquinazolone (1 mol equiv.), acetic acid-free LTA (1.05—1.1 mol equiv.), and dry dichloromethane (1 ml/100 mg, *N*-aminoquinazolone) containing the alkene (1.5—3.5 mol equiv.) and trifluoroacetic acid (1—6 mol equiv.) at room temperature.

Aziridination of Allyl Chloride.—The procedure in ref. 7*b* was followed using (**1**) (0.5 g), LTA (1.23 g), allyl chloride (0.303 g), and TFA (0.9 g) in dichloromethane (5 ml). The *aziridine* (**10**) (0.634 g, 85%) was obtained as colourless crystals, m.p. 87—89 °C (from ethanol) (Found: C, 58.95; H, 5.15; N, 15.45. $C_{13}H_{14}ClN_3O$ requires C, 59.2; H, 5.35; N, 15.9%); δ 8.15 (ddd, *J* 8.1, 1.5, and 0.5 Hz, 5-H), 7.69 (ddd, *J* 8, 7.4, and 1.5 Hz, 7-H), 7.62 (ddd, *J* 8, 1.4, and 0.6 Hz, 8-H), 7.42 (ddd, *J* 8.1, 7.4, and 1.4 Hz, 6-H), 4.14 (dd, *J* 11.5 and 4.8 Hz HC*H*Cl), 3.61 (dd, *J* 11.5 and 6.8 Hz, *H*CHCl), 3.46 (dddd, *J* 7.6, 6.8, 5.3, and 4.8 Hz, C*H*CH_2Cl), 3.08 (dq, *J* 17 and 7.3 Hz, *H*$CHCH_3$), 3.05 (dq, *J* 17 and 7.3 Hz, HC*H*CH_3), 2.72 (dd, *J* 7.6 and 1.6 Hz, aziridine *H*CH *cis* to quinaz.), 2.58 (dd, *J* 5.3 and 1.6 Hz, aziridine HC*H trans* to quinaz.), and 1.42 (t, *J* 7.3 Hz, CH_2CH_3); $\nu_{max.}$ 1 665s and 1 598s cm^{-1}.

When the above reaction was carried out in the absence of TFA, no aziridine (**10**) was obtained: the major product,

* In a competition experiment, oxidation of (**1**) with either LTA or $PhI(OAc)_2$ in the presence of methyl acrylate and α-methylenebutyrolactone gave the same ratio of aziridines in each case.

† It will be noted that trifluoroacetic acid is a byproduct in oxidations using LTTFA and $PhI(OCOCF_3)_2$ and the small yields of aziridine (**10**) obtained using these oxidants could derive at least in part from protonation of the quinazolone by the TFA formed as the reaction proceeds.

‡ At the time this proposal was made, the aziridinating species was believed to be the *N*-nitrene.

§ Aziridination of (*E*)-butene by oxidation of (**6**) with LTA gives a 1.2:1 ratio of aziridine stereoisomers in the absence of TFA and a 1:4 ratio of the same stereoisomers in the presence of TFA.[14]

isoluble in and separated by trituration with ice-cold ether, was the deaminated quinazolone (**14**) (77%).

Aziridination of Hex-1-ene.—The above procedure was followed using (**1**) (0.5 g), LTA (1.23 g), hex-1-ene (0.33 g), and TFA (0.9 g) in dichloromethane (5 ml). Chromatography of the crude product over silica with ethyl acetate–light petroleum (1:3) as eluant gave the trifluoroacetate (**13**) as an unstable oil (0.11 g, 11%); δ(90 MHz) 8.15 (d, *J* 8 Hz, 5-H), 7.2 (m, 6-, 7-, and 8-H), 5.5 (m, NH and *H*COCOCF$_3$), 2.6—3.0 (m, CH$_2$NH), 2.9 (q, *J* 7 Hz, C*H*$_2$CH$_3$), 1.3 (t, *J* 7 Hz, CH$_3$), and 1.8—0.8 [m, (CH$_2$)$_3$CH$_3$]; $\nu_{max.}$ 3 208w, 1 785s, 1 675s, and 1 600s cm^{-1}; *m/z* (%) 385 (*ca.* 1%), 289 (13), 258 (85), 244 (73), 216 (90), 203 (91), 202 (98), 200 (25), 190 (33), 176 (50), 175 (100), 174 (97), 173 (92), 160 (30), 120 (46), 103 (47), and 102 (47).

Further elution with the same solvent mixture gave the *aziridine* (**12**) (64%) as colourless crystals, m.p. 65—66 °C (from ethanol) (Found: C, 70.7; H, 8.1; N, 15.3. C$_{16}$H$_{21}$N$_3$O requires C, 70.8; H, 7.8; N, 15.5%); δ 8.18 (ddd, *J* 8, 1.5, and 0.6 Hz, 5-H), 7.67 (ddd, *J* 8.2, 6.8, and 1.5 Hz, 7-H), 7.62 (ddd, *J* 8.2, 1.5, and 0.6 Hz, 8-H), 7.40 (ddd, *J* 8, 6.8, and 1.5 Hz, 6-H), 3.11 (dq, *J* 16.5 and 7.4 Hz, *H*CHCH$_3$), 3.02 (dq, *J* 16.5 and 7.4 Hz, HC*H*CH$_3$), 2.82 (m, aziridine C*H*CH$_2$), 2.43 (dd, *J* 5.8 and 1.8 Hz, aziridine *H*CH *trans* to quinaz.), 2.38 (dd, *J* 7.8 and 1.8 Hz, aziridine HC*H cis* to quinaz.), 2.3—1.3 [m, (CH$_2$)$_3$], 1.43 (t, *J* 7.4 Hz, CH$_2$C*H*$_3$), and 0.95 [t, *J* 7 Hz, (CH$_2$)$_3$C*H*$_3$]; $\nu_{max.}$ 1 665s and 1 595s cm^{-1}.

When the above reaction was carried out in the absence of TFA, the aziridine (**12**) was isolated in 11% yield: the major product obtained after chromatography on silica and elution with ethyl acetate–light petroleum (1:3) was the deaminated quinazolone (**14**) (62%). When the same reaction was carried out using only 0.54 g (1.8 mol equiv.) of TFA, the isolated products were the trifluoroacetate (**13**) (5%), the aziridine (**12**) (37%), and the deaminated quinazolone (**14**) (27%).

Attempted Aziridination of (**16**).—3-Chloro-2-diethoxyphosphorylpropene (**16**) was prepared by the method of Welsh *et al.*[12] Using the above procedure, (**1**) 0.5 g), LTA (1.23 g), (**16**) (1.29 g), and TFA (1.8 g) were allowed to react in dichloromethane (5 ml). Trituration of the crude reaction product with cold light petroleum gave the *chloroketone* (**19**) (71%) as colourless crystals, m.p. 116—119 °C (from ethanol) (Found: C, 55.5; H, 5.05; N, 14.5. C$_{13}$H$_{14}$ClN$_3$O$_2$ requires C, 55.8; H, 5.05; N, 15.0%); δ(90 MHz) 8.15 (d, *J* 8 Hz, 5-H), 7.8—7.25 (m, 6-, 7-, and 8-H), 5.9 (t, *J* 6 Hz, exch. D$_2$O, NH), 4.15 (d, *J* 6 Hz, NHC*H*$_2$CO), 4.15 (s, COCH$_2$Cl), 3.0 (q, *J* 7 Hz, C*H*$_2$CH$_3$), and 1.31 (t, *J* 7 Hz, CH$_2$C*H*$_3$); $\nu_{max.}$ 3 280w, 1 710s, 1 665s, and 1 595s cm^{-1}. Repetition of the above reaction in the absence of TFA gave the deaminated quinazolone (**14**) (68%) isolated by trituration using ice-cold ether.

Aziridination of Allyl Acetate.—Using the procedure above, (**1**) (0.5 g), LTA (1.23 g), allyl acetate (0.4 g), and TFA (0.9 g), were allowed to react in dichloromethane (5 ml). The *aziridine* (**20**) was obtained (82%) as colourless crystals, m.p. 96—97 °C (from ethanol) (Found: C, 62.6; H, 5.6; N, 14.45. C$_{15}$H$_{17}$N$_3$O$_3$ requires C, 62.7; H, 5.9; N, 14.6%); δ 8.17 (ddd, *J* 8, 1.4, and 0.6 Hz, 5-H), 7.7 (ddd, *J* 8.1, 7.4, and 1.4 Hz, 7-H), 7.62 (ddd, *J* 8.1, 1.3, and 0.6 Hz, 8-H), 7.42 (ddd, *J* 8, 7.4, and 1.3 Hz, 6-H), 4.45 (dd, *J* 12.1 and 4.8 Hz, *H*CHOAc), 4.38 (dd, *J* 12.1 and 5.7 Hz, HC*H*OAc), 3.28 (dddd, *J* 8.4, 5.7, 5.7, and 4.8 Hz, C*H*CH$_2$OAc), 3.09 (2 × dq, *J* 18 and 7.1 Hz, C*H*$_2$CH$_3$), 2.66 (dd, *J* 8.4 and 1.85 Hz, aziridine *H*CH *cis* to quinaz.), 2.58 (dd, *J* 5.7 and 1.85 Hz, aziridine HC*H trans* to quinazolone), 2.15 (s, OCOCH$_3$), and 1.44 (t, *J* 7.1 Hz, CH$_2$C*H*$_3$).

N.m.r. Spectrum of N-*Acetoxyaminoquinazolone* (**2**) *in the Presence of TFA.*—A solution of (**2**) in CDCl$_3$ was prepared by oxidation of (**1**) at −20 °C as described previously[8] and freed from lead diacetate by filtration through a cotton wool plug. The solution was cooled to −40 °C and TFA added (3 mol equiv.). The n.m.r. of this solution was measured at −40 °C, without any intermediate warming, and had δ(CDCl$_3$) 11.00 (s, NH), 8.37 (d, *J ca.* 8 Hz, 5-H), 8.08 (t, *J ca.* 8 Hz, 7-H), 7.84 (d, *J ca.* 8 Hz, 8-H), 7.83 (t, *J ca.* 8 Hz, 6-H), 3.44 (10 lines, m, CH$_2$), 2.18, 2.19 (2 × s, OCOCH$_3$ and HOCOC*H*$_3$), and 1.57 (t, *J* 6 Hz, CH$_3$): for comparison, (**2**) in the absence of TFA has δ(CDCl$_3$) 10.98 (s, NH), 8.25 (ddd, *J* 8, 1.4, and 0.6 NHz, 5-H), 7.84 (ddd, *J* 8, 7.4, and 1.4 Hz, 7-H), 7.71 (ddd, *J* 8, 1.4, and 0.6 Hz, 8-H), 7.52 (ddd, *J* 8, 7.4, and 1.4 Hz, 6-H), 3.19 (dq, *J* 17 and 7 Hz, CH*H*CH$_3$), 3.03 (dq, *J* 17 and 7 Hz, C*H*HCH$_3$), 2.15 (s, OCOCH$_3$ and HOCOC*H*$_3$), and 1.43 (t, *J* 7 Hz, CH$_2$C*H*$_3$).

Aziridination of Allyl Chloride using Pre-formed N-*Acetoxyaminoquinazolone* (**2**).—A solution of (**2**) in dichloromethane (6 ml) was obtained at −20 °C by oxidation of *N*-aminoquinazolone (400 mg) with LTA (1.03 g) as described previously.[8] This solution, held at −20 °C (containing suspended lead diacetate), was added dropwise with stirring to a solution of allyl chloride (486 mg) and TFA (1.45 g) in dichloromethane (2 ml) held at 0 °C. The mixture was allowed to warm to room temperature, when saturated aqueous sodium hydrogen carbonate was added and the insoluble solids separated. The dichloromethane layer was separated, washed with water, dried, and evaporated to give the aziridine (**10**) as a crystalline solid (513 mg, 92%). Examination of this solid by n.m.r. at 400 MHz showed that it contained *ca.* 8% of the deaminated quinazolone (**14**).

Acknowledgements

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