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AZIRIDINATION OF ALKENES BY 3-AMINO-2-ETHYLQUINAZOLIN-3H-4-ONE AND LEAD TETRA-ACETATE-TRIFLUOROACETIC ACID

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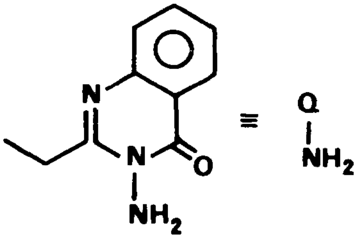
SUMMARY: A number of alkenes undergo aziridination in good yield by oxidative addition of the title N-aminoquinazolone (1) only in the presence of TFA.

The title N-aminoquinazolone (1) is one member of a family of N-aminoheterocyclic compounds whose oxidation with lead tetraacetate (LTA) in the presence of alkenes give aziridines.[1] Hitherto, the reactive intermediates in these oxidations have been assumed to be N-nitrenes but recent work has indicated that, at least in oxidation of N-aminoquinazolones, other species are implicated.[2]

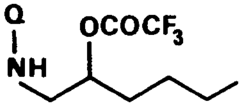
These oxidative additions of N-aminoquinazolones bring about aziridination of both electron-rich and electron-deficient alkenes often in high yields in the presence of excess of the alkenes. However, the yields of aziridines with 'electron sufficient' alkenes, e.g. mono-alkylsubstituted ones, are invariably poor.[3]

We find that the yields of aziridines or their transformation products from these unreactive alkenes can be greatly increased by carrying out the oxidative additions in the presence of trifluoroacetic acid (TFA). Moreover, these yields have been obtained using only small excesses of the alkenes in question. Thus oxidation of (1) in the presence of allyl chloride (1.5 mol equiv.) gave <10% of the aziridine (2) from n.m.r. examination of the crude reaction mixture. In the presence of (TFA) (6 mol equiv.), however, a 90% yield of aziridine (2)



(1)

(2) R = CH_2Cl
(3) R = $(CH_2)_3CH_3$



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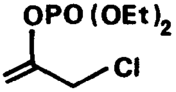

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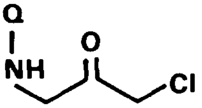

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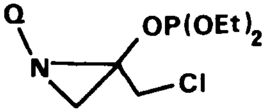

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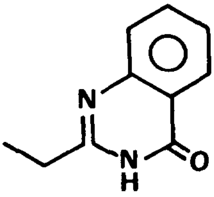

(8)

was isolated, m.p. 87-89 °C; n.m.r. ($CDCl_3$; 300 MHz) includes δ4.14 (dd, *J* 11.5 and 4.8 Hz, HCHCl), 3.61 (dd, *J* 11.5 and 6.8 Hz, HCHCl), 3.46 (dddd, *J* 7.6, 6.8, 5.3, and 4.8 Hz, $CHCH_2Cl$), 3.08 (dq, *J* 17 and 7.3 Hz, $HCHCH_3$), 3.05 (dq, *J* 17 and 7.3 Hz, $HCHCH_3$), 2.72 (dd, *J* 7.6 and 1.6 Hz, azir. CHH *trans* to CH_2Cl), 2.58 (dd, *J* 5.3 and 1.6 Hz, azir. CHH *cis* to CH_2Cl), 1.43 (t, J 7.3 Hz, CH_3).

Oxidation of (1) in the presence of hex-1-ene gave aziridine (3) in 11% yield which was raised to 64% when TFA (3 mol equiv.) was present: in addition, the ring-opened trifluoroacetate (4) (11%) was also isolated.[4] Similarly, oxidation of (1) in the presence of the diethoxyphosphoryl-substituted allyl chloride (5)[5] (2 mol equiv.) gave the chloroketone (6) (71%; isolated), m.p. 117-119 °C. Presumably this chloroketone (6) is formed by ring-opening of the initially formed aziridine (7). In the absence of TFA, no chloroketone (or aziridine (7)) is formed.

The major product from the above oxidations of (1) in *absence* of TFA is the de-aminated product (8). Formation of (8) is believed to result from reaction of unchanged (1) with its oxidation product (previously thought to be the *N*-nitrene). It is conceivable that formation of (8) is suppressed in the presence of TFA by the reduced reactivity of the amino group on the above unchanged (1) when this molecule is protonated (either on N-1 or the carbonyl oxygen).

In any case, the species which is formed from LTA oxidation of (1) in the presence of TFA is clearly different from that formed in its absence and is remarkably more selective. Thus oxidation of (1) in a mixture of α-methylene-γ-butyrolactone and methyl methacrylate (1:1) gives a 2:1 mixture of the corresponding aziridines in the *absence* of TFA but in the presence of TFA only aziridination of methyl methacrylate occurred from examination of the n.m.r. spectrum of the crude reaction mixture.

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References and Notes

1. R.S. Atkinson 'Azides and Nitrenes', ed. E.F.V. Scriven, Academic Press, Orlando, Florida, 1984.
2. R.S. Atkinson and B. Kelly, unpublished work.
3. D.J. Anderson, D.C. Horwell, T.L. Gilchrist, and C.W. Rees, *J. Chem. Soc., (C)*, 1970, 576; R.S. Atkinson and C.W. Rees, *J. Chem. Soc., (C)*, 1969, 772.
4. Using less TFA (1.8 mol equiv.), the isolated yields of (3) and (4) were 37% and 5% respectively: 27% of de-aminated quinazolone (8) was also obtained.
5. S.C. Welch, S.-M. Assercq, and J.P. Loh, *Tetrahedron Letters*, 1986, 1115.

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