Aziridination of Cyclohex-2-en-1-ol and Geraniol: Comparison with Epoxidation

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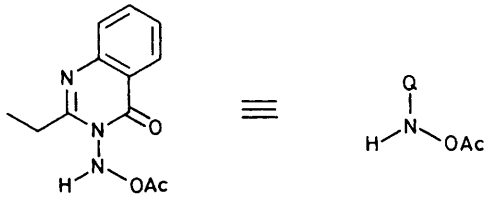
Aziridination of cyclohex-2-en-1-ol with 3-acetoxyamino-2-ethylquinazolone (**1**) is highly stereoselective, and reaction with geraniol is highly regioselective for the allylic alcohol double bond; comparisons are made with the corresponding reactions of peracids.

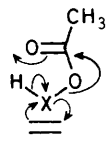
We have shown that the *N*-acetoxyaminoquinazolone (**1**) is an effective aziridinating agent for alkenes.[1] It was suggested that the mechanism for this aziridination (**2**) might be analogous to that accepted for peracetic acid oxidation of alkenes to give epoxides.

Seeking support for this analogy, we carried out the aziridinations of cyclohexenol (**3**) with (**1**). It is well known that epoxidation of (**3**) with peracids leads stereoselectively to the *syn*-epoxide (**4**); this has been attributed to hydrogen bonding in the transition state between the peracid and the OH group.[2]

Aziridination of (**3**) was carried out either by using solutions of (**1**) or by lead tetra-acetate (LTA) oxidation of the *N*-aminoquinazolone (**6**) in the presence of cyclohexenol (**3**) (3 mol. equiv.). The major product (**7**), m.p. 99—102 °C, isolated in 70% yield, was the *syn*-stereoisomer (**7**) with J(H1)(H2) = 4.5 Hz, J(H1)(H6) = 9 Hz, and J(H1)(H6′) = 6 Hz in its n.m.r. spectrum.

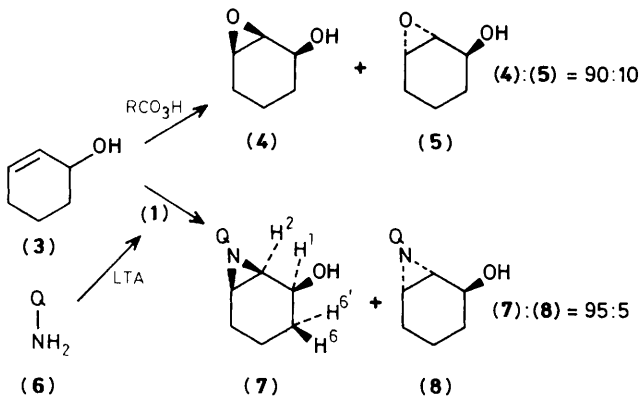


(**1**)



epoxidation X = O
aziridination X = NQ

(**2**)



From a similar reaction of cyclohexenyl acetate (**9**), the only aziridine isolated was (**10**) (7%, m.p. 120—123 °C) having J(H1)(H2) = *ca.* 1 Hz in its n.m.r. spectrum.[3]

The amount of the minor stereoisomer (**8**) produced in the aziridination of cyclohexenol (**3**) was assayed by acetylation of the reaction mixture; n.m.r. examination of this product revealed only 5% of the acetate (**10**) to be present.

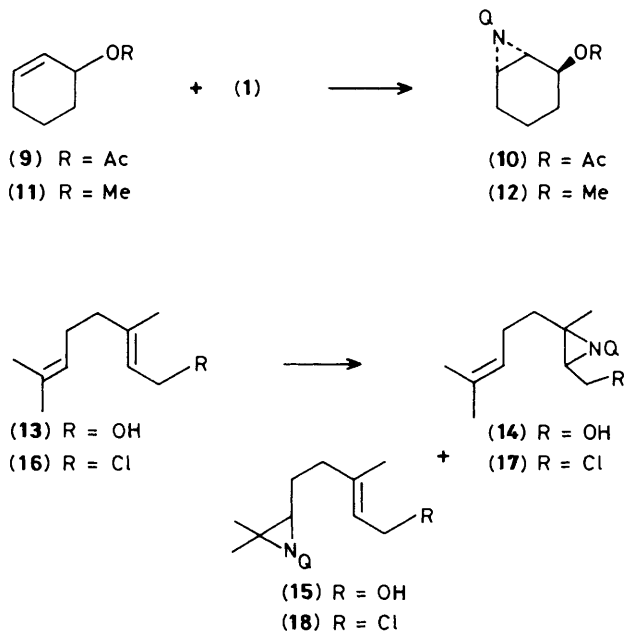
The importance of hydrogen bonding for efficient *syn*-aziridination of (**3**) was shown in the reaction of the derived methyl ether (**11**) with (**1**); only the *anti*-stereoisomer was isolated [19%, m.p. 107—109 °C, J(H1)(H2) = *ca.* 1 Hz].

These aziridination results are analogous to those found for epoxidation of (**3**), (**9**), and (**11**),[2] except that aziridination of (**9**) and (**11**) proceeds far more stereoselectively *anti* (but in poorer yield) than the corresponding epoxidations.

Aziridination of geraniol (**13**) with the *N*-acetoxyaminoquinazolone (**1**) or by LTA oxidation of (**6**) gave (**14**) (76%, m.p. 128—130 °C) and (**15**) (7%). Geranyl chloride (**16**), by contrast, is aziridinated preferentially on the 6,7-bond [ratio (**17**):(**18**) = 1:6].

Epoxidation of geraniol with peracids is not very regioselective: *m*-chloroperbenzoic acid gives a 2:1 ratio of epoxides from attack on the 6,7- and 2,3-double bonds respectively.[4]

Both the greater stereoselectivity in the aziridination of (**3**) and the higher regioselectivity in aziridination of geraniol with (**1**) can be rationalised by assuming stronger hydrogen bonding between the latter and the hydroxy group in the transition state for aziridination.



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3 These values of J(H1)(H2) of 4.5 Hz [for (**7**)] and 1 Hz [for (**10**) and (**11**)] are close to those found for 2,3-epoxides of cyclohexene-1-carboxylates of known configuration: S. G. Davies and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1977, 572.
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