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AZIRIDINE-AZIRINE TRANSFORMATION BY 1,2-ELIMINATION *via* AN AZIRIDINYL CARBANION INTERMEDIATE

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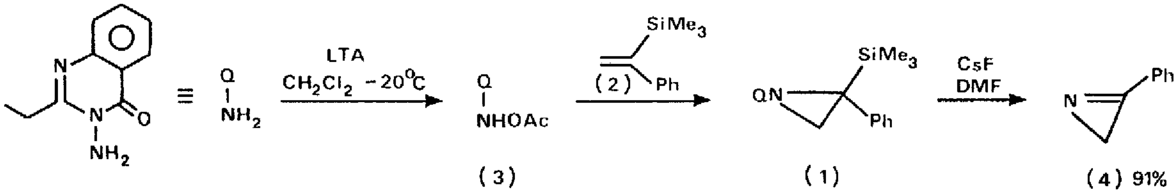
Summary: Desilylation of aziridine (5) by treatment with cesium fluoride in dry dimethylformamide in the presence of benzaldehyde followed by oxidation with manganese dioxide gives the benzoylaziridine (11) in 80% yield: in the absence of benzaldehyde, the presumed aziridinyl carbanion intermediate (9) gives the aziridine (7) (58%).

Of the known methods for preparing azirines, 1,2-elimination from a suitably substituted aziridine is surprisingly absent.[1] We have found that trimethylsilyl-substituted aziridine (1), prepared by aziridination of alkenylsilane (2) using *N*-acetoxyaminoquinazolone (3), gives 2-phenylazirine (4) in excellent yield.[2]



2*H*-Azirines, unsubstituted at C-3, are considerably more reactive than those, e.g. (4), substituted at this position. It was of interest, therefore, to apply the conditions which bring about 1,2-elimination in (1) to the isomeric aziridine (5) (Scheme) from which the reactive azirine (6) would be anticipated as the first-formed product.

Aziridine (5) was prepared by aziridination of *E*-trimethyl-2-phenylethenylsilane with a solution of (3) and isolated in 86% yield as a colourless oil after chromatography over silica. Its n.m.r. spectrum shows the presence of both invertomers at the aziridine ring nitrogen (ratio 1.8:1) with the major invertomer having the quinazolone ring and trimethylsilyl group *cis*.

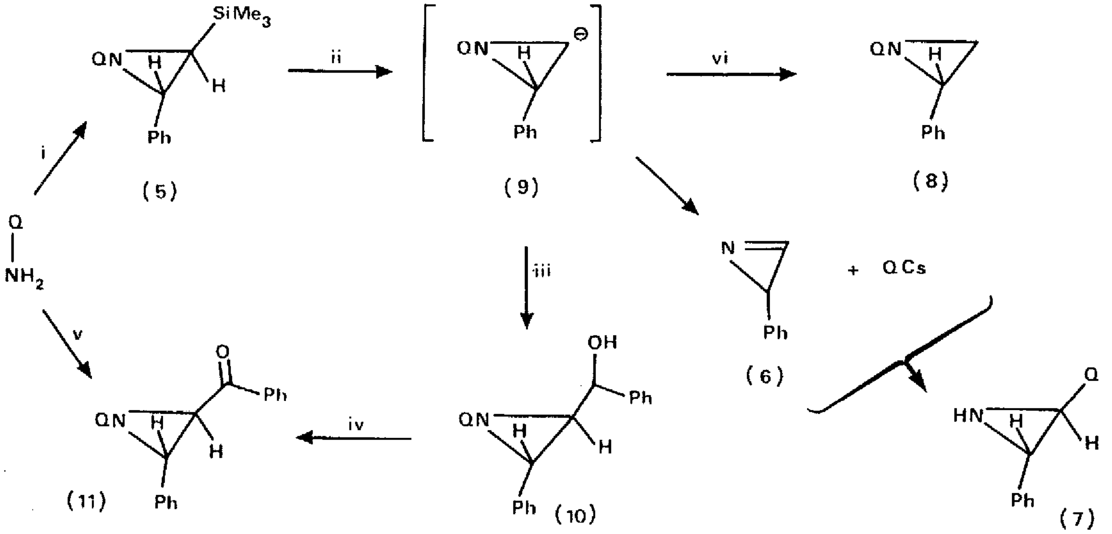
Treatment of (5) with cesium fluoride in dimethylformamide for 4h. at room temperature gave two major products which were separated by silica chromatography. The slower-running material m.p. 122-125 °C was isolated in 58% yield and identified as the aziridine (7) (Scheme). Aziridine (7) shows the presence of two invertomers at nitrogen (ratio 4:1) in its n.m.r. spectrum at -55 °C with the major invertomer (Ph and N*H* *cis*) having δ (400MHz) 8.17, 7.75, 7.61, and 7.47-7.32 (quinaz. and phenyl *H*), 4.02 (dd, *J* 7.7 and 2.1 Hz, C*H*Ph), 3.28 (dd, *J* 9.4 and 2.1 Hz, C*H*Q), 3.26 (dq, *J* 17 and 7 Hz, $\underline{H}CHCH_3$), 2.91 (dq, *J* 17 and 7 Hz, $HC\underline{H}CH_3$), 2.03 (dd, *J* 9.4 and 7.7 Hz, (exch. D_2O,) NH), and 1.36 (t, *J* 7 Hz, $CH_2C\underline{H}_3$): the minor invertomer has δ 8.11, 7.75, 7.60, and 7.47-7.32 (quinaz. and phenyl *H*), 3.67 (dd, *J* 6.7 and 1.7 Hz, C*H*Q), 3.32 (dd, *J* 10.1 and 1.7 Hz, C*H*Ph), 3.97 (dq, *J* 17 and 7 Hz, $\underline{H}CHCH_3$), 2.79 (dq, *J* 17 and 7 Hz $HC\underline{H}CH_3$), 2.25(dd, *J* 10.1 and 6.7 Hz, (exch. D_2O), NH), and 1.30

(t, J 7 Hz, CH_2CH_3).

We suppose that the azirine (6) is an intermediate in the formation of this aziridine (7) and is attacked at the reactive unsubstituted 3-postion by the quinazolone anion.

The faster-running product from the desilylation of (5) was the aziridine (8)[3] (23%). A possible origin of this desilylation product would be from capture of the aziridinyl carbanion intermediate (9) by adventitious water. To test this possibility, the desilylation of (5) was carried out in the presence of benzaldehyde (3 mol equiv.). Oxidation of the labile product (10) directly with manganese dioxide gave the benzoylaziridine (11) (80% from (5)), identical with a sample prepared by direct aziridination of benzylidene acetophenone.

This sequence strongly suggests that the aziridinyl carbanion is long-lived enough to be captured by benzaldehyde but, in the absence of an electrophile, forms the azirine (6) by expulsion of the quinazolone anion.[4]



Scheme i. LTA, CH_2Cl_2, -20 °C then E-PhCH=CHSiMe$_3$, ii. CsF, DMF, 4h. 20 °C, iii. PhCHO, iv. MnO_2, CH_2Cl_2, v. LTA, CH_2Cl_2 PhCH=CHCOPh, vi. H_2O.

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