Aziridination of Vinylsilanes and Vinylstannanes: A New Synthesis of Azirines

Robert S. Atkinson and Brian J. Kelly

Department of Chemistry, Leicester University, Leicester LE1 7RH, U.K.

Aziridination of vinylsilanes and vinylstannanes with the *N*-acetoxyaminoquinazolone (**8**) gave aziridines (**1**)—(**7**): caesium fluoride in dimethylformamide brought about elimination of trimethylsilyl and quinazolone groups from (**1**) and (**2**) to give the corresponding azirines.

Relatively few 2- or 3-silyl-substituted aziridines are known[1] and a literature search revealed no 2- or 3-stannyl-substituted aziridines: the chemistry of these silyl-substituted aziridines, unlike that of silylepoxides[2] has not been investigated.

We have prepared aziridines (**1**)—(**7**) by reaction of *N*-acetoxyaminoquinazolone (**8**) with the corresponding vinylsilanes or vinylstannanes (Scheme 1). This aziridination method uses the preparation of (**8**), *in situ*, by oxidation of (**9**) with lead tetra-acetate in dichloromethane and subsequent addition of the vinylsilane or vinylstannane.[3] The aziridines (**1**)—(**7**) were isolated by flash chromatography over silica, mostly as crystalline solids (see Table 1).

The substituted vinylsilanes or vinylstannanes used to prepare (**2**), (**6**), and (**7**) were mixtures of stereoisomers and although, in each case, only one of the latter appeared to react, this presented problems in configurational assignment at C-2 and C-3 of the aziridine ring. Also, with the exception of (**4**) and (**5**), all these azirizines showed the presence of invertomers at the aziridine ring nitrogen in their n.m.r. spectra. Finally, it is clear that in some cases there is restricted rotation around the N–N bond within individual invertomers.[4]

A number of factors support the relative configuration at C-2 and C-3 shown in these aziridines. (i) The yield of (**6**) is such that it must be derived from the more abundant vinylstannane† which ^{117}Sn– and ^{119}Sn–vinyl H coupling constants show to have a (*Z*)-configuration. (ii) Nuclear Overhauser enhancements (n.O.e.) between the *ortho* protons of the aziridine ring phenyl and the aziridine ring proton in (**6**) support a *cis*-relationship between them. (iii) The pattern of chemical shift changes for aziridine ring protons and aziridine ring methyl groups in (**2**), (**6**), and (**7**) in the two invertomers at the aziridine ring nitrogen (see below) is consistent with addition to the (*Z*)-vinylsilane or vinylstannane in each case.

Assignment of the relative configuration at the aziridine ring nitrogen in the two invertomers is based on a deshielding of the aziridine ring proton when *cis* to the quinazolone and, conversely, shielding of the aziridine ring methyl when *cis* to the quinazolone.[5] The invertomer ratio change in going from (**6**) to (**7**) is consistent with the invertomer assignments made, as is the chemical shift variation of the quinazolone ring H-5 in the two invertomers in (**1**), (**2**), (**6**), and (**7**) with δ major (minor) at 8.26 (7.8), 7.88 (8.22), 8.18 (7.9), and 8.21 (7.98), respectively: evidently a phenyl group *cis* to the quinazolone ring brings about shielding of H-5 in the latter by ~0.3—0.4 p.p.m.

It seems likely from the invertomer ratios above‡ that there

Table 1. Aziridination products from vinylsilanes and vinylstannanes with *N*-acetoxyaminoquinazolone (**8**).

Product	% Yield	M.p./°C	Invertomer ratio *cis* : *trans* (Q : Si, Sn)
(**1**)	30	108—110	13 : 1
(**2**)	12	111—114	1 : 5
(**3**)	86	Oil	1.8 : 1
(**4**)	38	Oil	>50 : 1
(**5**)	28	53—56	>50 : 1
(**6**)	61	115—118	8 : 1
(**7**)	34	157—159	4 : 1

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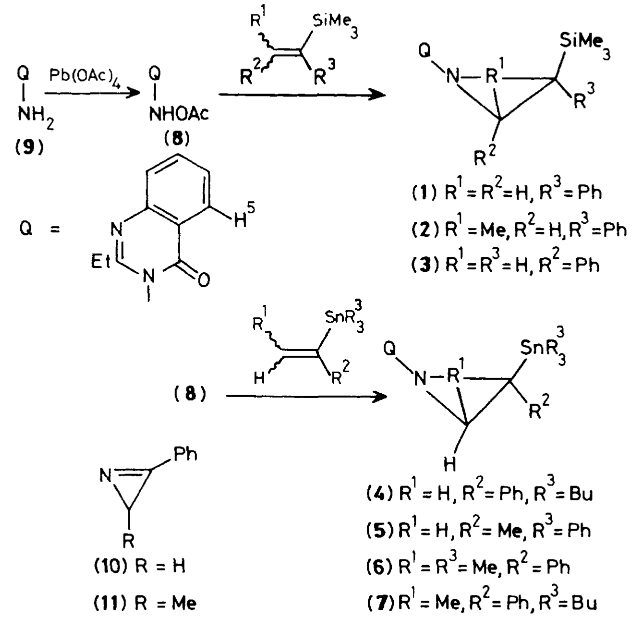
† This assumes stereospecific *cis*-addition in the aziridination which is always found to be the case.

‡ Evidence for an *N*-invertomer relationship between the two species present in the n.m.r. spectra of aziridines (**6**) and (**7**) is provided by a gross change in the invertomer ratio when crystalline samples of the aziridines are dissolved in $CDCl_3$ at −40 °C and their spectra measured at this temperature, *cf.* R. S. Atkinson and G. Tughan, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2987.



Scheme 1

is an attractive interaction between the quinazolone carbonyl oxygen and the tin atom which offsets the steric interactions present in (**4**)—(**7**).[6]

The yields of aziridines in addition to the vinylstannanes are sensitive to the bulk of the substituents on tin. We suspect that coplanarity of the phenyl group in (**4**), (**6**), and (**7**) with the double bond is hindered to an extent which depends upon the size of these substituents since coplanarity is known to be required for efficient aziridination of substituted styrenes.[7]§

The excellent yield of aziridine (**3**) (86%) derives from the fact that coplanarity of the phenyl ring and double bond is unimpaired.

When (**1**) was stirred for 5 h at room temperature in dimethylformamide with caesium fluoride, conversion to azirine (**10**) (91%) and the 2-ethylquinazolin-4(3*H*)-one took place. The formation of azirines by 1,2-elimination from suitably substituted aziridines is hardly known[8] and the mildness of the conditions used here is notable. A similar elimination occurred to give azirine (**11**) (61%) when aziridine (**2**) was treated with fluoride under the same conditions.

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§ The reactivity of only one double bond isomer in additions to (**2**), (**6**), and (**7**) can be explained similarly.

References

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2 'Silicon in Organic Synthesis,' ed. E. Colvin, Butterworths, London, 1981.

3 R. S. Atkinson and B. J. Kelly, *J. Chem. Soc., Chem. Commun.*, 1987, 1362; we found subsequently that, at least in the case of vinylsilanes, aziridination can be accomplished by direct addition of lead tetra-acetate and (**9**) to the alkene (see ref. 4).

4 Compare R. S. Atkinson and G. Tughan, *J. Chem. Soc., Perkin. Trans. 1*, 1987, 2797.

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