Tetrahedron Letters,Vol.24,No.38,pp 4153-4156,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

THE STEREOCHEMISTRY OF SOME S_E2' REACTIONS OF ALLYL- AND ALLENYLSILANES[1]

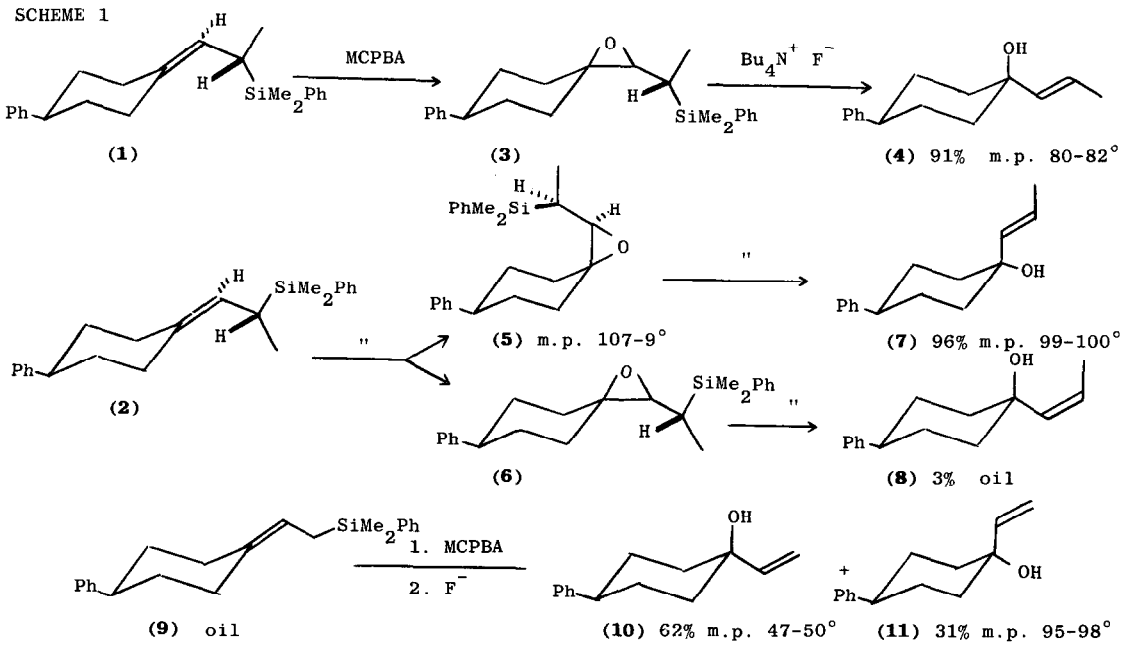
Ian Fleming* and Nicholas K. Terrett

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Summary—The S_E2' reactions of **1** and **2** with a range of electrophiles are predominantly *anti* in the allylsilane portion of the molecule, but this is offset, to a greater or lesser extent, by axial or equatorial preferences in the ring system.

In the preceding communication,[2] we describe the stereospecific synthesis of the allylsilanes (**1** and **2**). We now report the stereochemistry of their reactions with three representative electrophiles. Kumada[3] has shown that allylsilanes react in an overall *anti* manner with a variety of electrophiles, but in his reactions the only stereochemical constraint was provided by the allylsilane group. In our reactions, the *anti* selectivity is again apparent, but it is either reinforced by or opposed to the axial or equatorial preference the electrophiles inherently show towards the ring system.

SCHEME 1

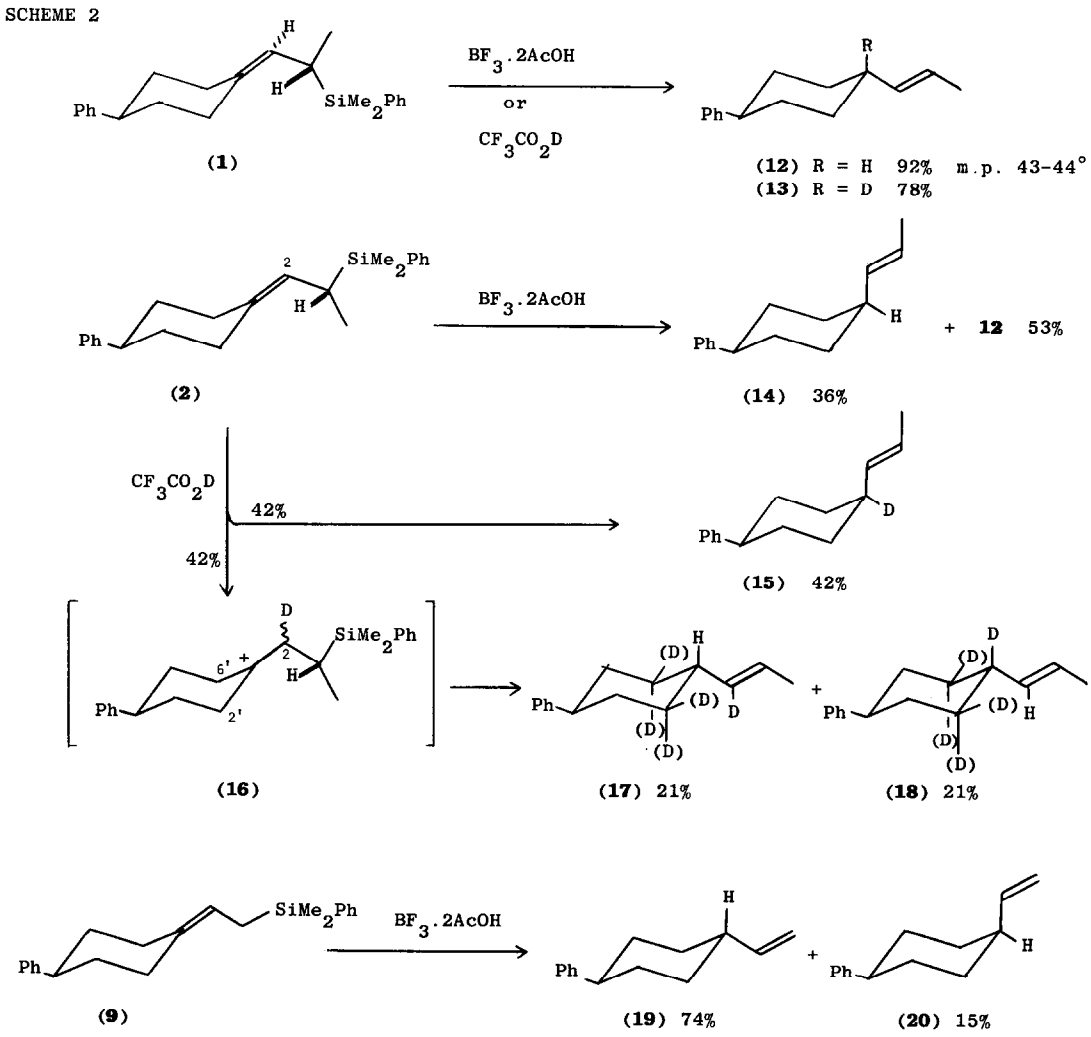


Epoxidation (Scheme 1).—Epoxidation was very well behaved. The epoxides (**3**, **5**, and **6**) were isolable, but it was convenient simply to convert them directly to the allylic alcohols (**4**, **7**, and **8**). All the reactions were cleanly *anti* overall, and, although there was a small preference for axial attack,[4] the overall stereochemistry was *very largely determined by the allylsilane group*. The small axial preference was supported by the corresponding reaction of the allylsilane (**9**),

which gave twice as much axial attack as equatorial; in this allylsilane, the ring system alone is responsible for the stereochemical bias.

Protonation (Scheme 2).—Protonation of the allylsilane (**1**) was cleanly *anti* and axial, but protonation of the other allylsilane (**2**) gave a mixture of products (**12** and **14**). Deuteronation clarified the picture: the allylsilane (**1**) was straightforward (**1**→**13**), and so was equatorial-*anti* attack on the other allylsilane (**2** → **15**). The anomalous (apparently *syn*) product (**12** in protonation) was revealed to have arisen by a different pathway, which we have observed before[5] with

SCHEME 2

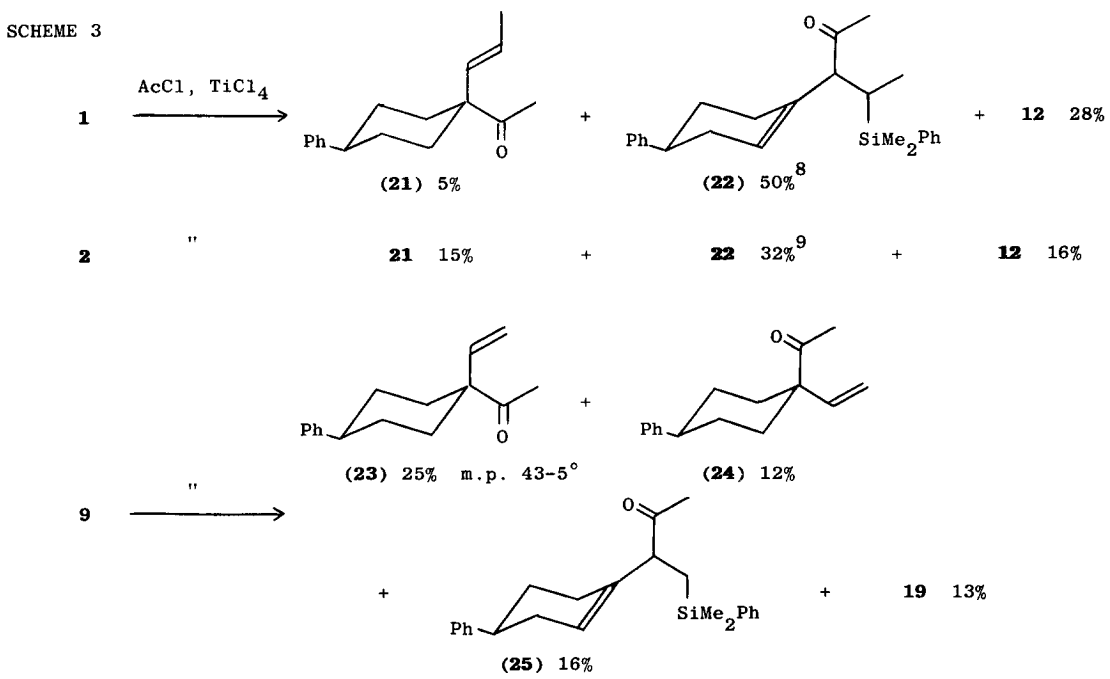


3,3-disubstituted allylsilanes: the deuteron has attacked C-2 of the allyl system to give a tertiary cation (**16**). This cation can lose protons (and regain deuterons) from C-2' and C-6', and it can also undergo hydride or deuteride shift and loss of the silyl group to give the alkenes (**17** and **18**), each of which was a mixture of mono-, di-, tri-, tetra-, and penta-deuterated species.[6] The implication is that axial attack is again inherently preferred, but that when the axial preference of the ring system opposes the *anti* selectivity of the allylsilane group, the molecule (**2**)

finds an alternative reaction, in which stereospecificity is lost. In support of this analysis, we found that the allylsilane (**9**) was protonated largely from the axial direction.[7]

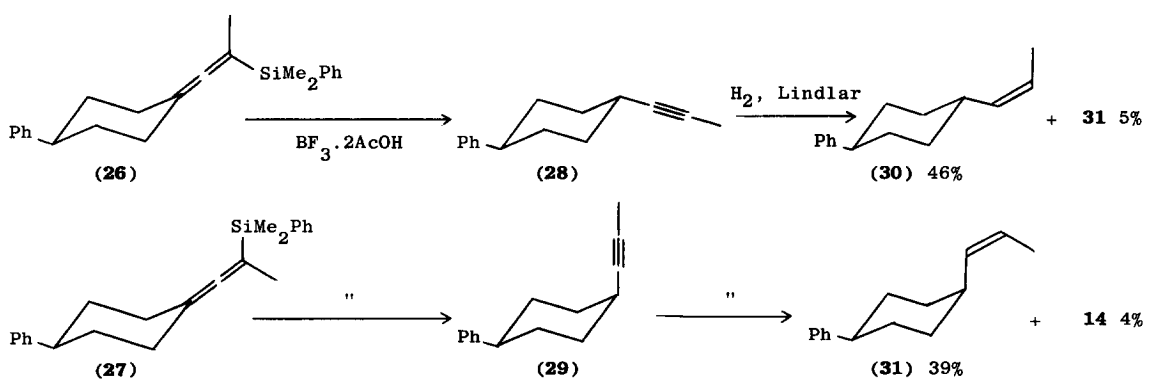
Acylation (Scheme 3).—Acylation was even less straightforward: S_E2' reaction (**1** or **2** → **21**) was only a minor pathway, and acylation on C-2 and protodesilylation were major pathways. In so far as stereochemical control is evident, equatorial acylation appears to be favoured, so that the

SCHEME 3



allylsilane (**2**) gave a better yield of **21** than the allylsilane (**1**), because equatorial attack is *anti* in this case. An equatorial preference is also evident in the corresponding reaction of the allylsilane (**9**), which gave twice as much equatorial (**23**) as axial (**24**) attack.

Protodesilylation of allenylsilanes (Scheme 4).—The allenylsilanes[2] (**26** and **27**) were protodesilylated in rather poor yield, but the stereochemistry was very largely *anti*: to analyse the



stereochemistry, we reduced the acetylenic products (**28** and **29**) to the alkenes (**30** and **31**), and oxidised the alkenes to the known[10] carboxylic acids. These reactions appear to be the first ex-

amples of the straightforward protodesilylation of allenylsilanes.[11] The electrophilic substitution of this class of compounds has been studied to some extent, mostly with carbon electrophiles,[12] but the stereochemistry has not been investigated before. The poor yields are perhaps not too surprising in view of some of the unusual reaction which allenylsilanes show.[11,12]

In conclusion, we have supported Kumada's and Wetter's results, as well as some inconclusive ones of our own,[13] which indicate that the S_E2' reaction is *anti* selective. In all our work, we have seen little sign of any *cis*-alkene in the product mixtures, presumably because the allylsilanes react from a conformation (**1** or **2**) in which the hydrogen is the only group small enough to eclipse the double bond (as Kumada found[3] for his Z-allylsilanes). Furthermore, we are now in a better position to assess how powerful the *anti* selectivity is when it is in competition with other constraints. In particular, we note that, whereas protodesilylation and acylation can easily be led astray, bridging electrophiles such as peracid and osmium tetroxide[2] are very selective for an overall *anti* reaction. The clean formation of a *trans* double bond in an *anti* reaction augurs well for the usefulness of the S_E2' reaction in the control of stereochemistry in open-chain reactions.

NOTES and REFERENCES

1. No reprints available.
2. I. Fleming and N. K. Terrett, preceding communication.
3. T. Hayashi, M. Konishi, H. Ito, and M. Kumada, *J. Am. Chem. Soc.*, **104**, 4962 (1982); T. Hayashi, M. Konishi, and M. Kumada, *ibid.*, 4963; T. Hayashi, H. Ito, and M. Kumada, *Tetrahedron Lett.*, **24**, 4605 (1983); see also H. Wetter and P. Scherer, *Helv. Chim. Acta*, **66**, 118 (1983), and G. Wickham and W. Kitching, *J. Org. Chem.*, **48**, 612 (1983).
4. Although the yield of **4** was lower than that of **7**, there was no trace of any of the other three allylic alcohols in the product from **1**, whereas the small amount of **8** was easily detectable in the product from **2**.
5. I. Fleming, D. Marchi, and S. K. Patel, *J. Chem. Soc., Perkin Trans. 1*, 2518 (1981).
6. The analysis of these mixtures was carried out by inspection of ^1H-, ^2H-, and ^{13}C-NMR and mass spectra. The numbers are not exact (for example there ought to be some product arising from hydride shift in **16** to the equatorial face giving a product like **15** but with a deuteron on C-2; judging by the spectra, there was very little such product, less than 3%).
7. Deuteronation with CF_3CO_2D gave products analogous to **13**, **17**, and **18**, in 41% yield, and in a ratio of 74:13:13, respectively.
8. A mixture of at least three diastereoisomers.
9. A single crystalline diastereoisomer, m.p. 74-76°.
10. H. E. Zimmerman and H. J. Giallombardo, *J. Am. Chem. Soc.*, **78**, 6259 (1956).
11. M. Grignon-Dubois, J.-P. Pillot, J. Dunogues, N. Duffaut, R. Calas, and B. Henner, *J. Organomet. Chem.*, **124**, 135 (1977).
12. R. L. Danheiser and D. J. Carini, *J. Org. Chem.*, **45**, 3925 (1980); R. L. Danheiser, D. J. Carini, and A. Basak, *J. Am. Chem. Soc.*, **103**, 1604 (1981); A. Jellal and M. Santelli, *Tetrahedron Lett.*, **21**, 4487 (1980); J. P. Dulcere, J. Grimaldi, and M. Santelli, *ibid.*, **22**, 3179 (1981); J.-P. Pillot, B. Bennetau, J. Dunogues, and R. Calas, *ibid.*, 3401.
13. B.-W. Au-Yeung and I. Fleming, *Tetrahedron*, **37** Supplement 1, 13 (1981); M. J. Carter, I. Fleming, and A. Percival, *J. Chem. Soc., Perkin Trans. 1*, 2415 (1981); and I. Fleming and R. V. Williams, *ibid.*, 684 (1981).

(Received in UK 6 July 1983)