The Stereochemistry of Osmylation, Epoxidation, and Methylenation of Allylsilanes†

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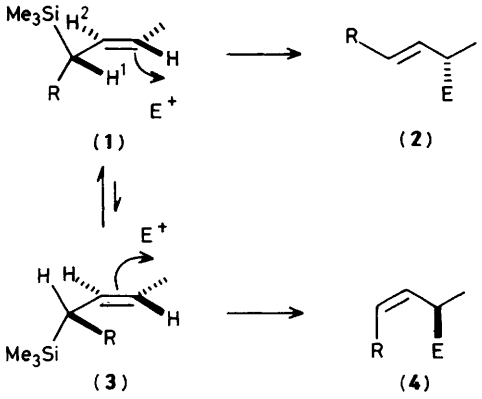
The stereochemistry of attack on an allylsilane is more selective when the substituent on the chiral centre carrying the silyl group is larger than a methyl group, as shown by the reactions of the allylsilanes (**5**) and (**12**) with osmium tetroxide, *m*-chloroperbenzoic acid, and Yamamoto's methylenation reagent.

Electrophiles usually attack open-chain allylsilanes to give overall *anti* S_E2' reactions, and the probable reason is that attack takes place in the more abundant conformation (**1**) on the surface *anti* to the large, electron-donating silyl group.[1—3] The result is an alkene (**2**) with a *trans* double bond. However, there is often a small amount of product (**4**) with a *cis* double bond, which is presumably produced by attack on the less abundant conformation (**3**).[2—4] Recently, Vedejs and McClure found that the reaction of osmium tetroxide on the allylsilane (**5a**) was anomalous in giving more of the diol (**7a**)

† No reprints available.



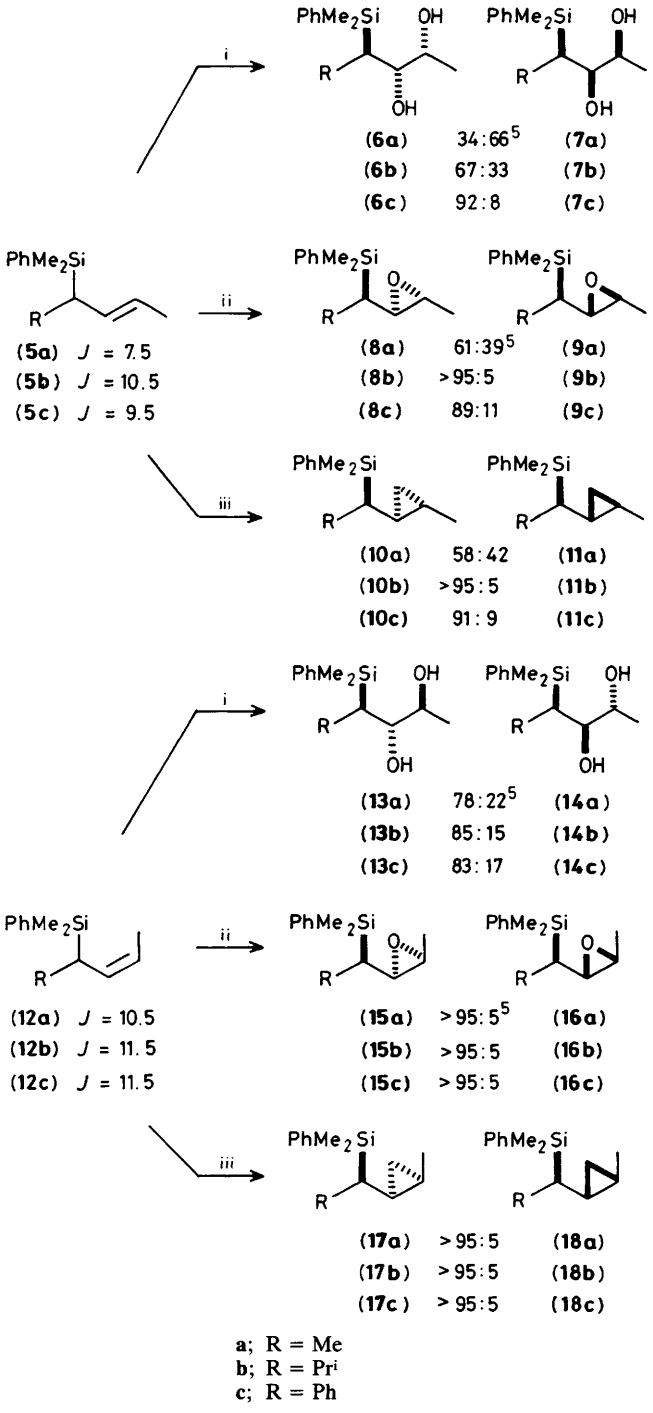
than of the diol (**6a**).[5] They explained their result by saying that osmium tetroxide is a large electrophile, and that the attack on the upper surface of the conformation (**3**) is less hindered than attack on the lower surface of conformation (**1**), where the R group hinders the approach of the electrophile. Vedejs and McClure actually use slightly different pictures, from those used here, and so do Houk and his co-workers.[6] The equilibrium conformation of allylsilane itself has the dihedral angle subtended by the silyl group with respect to the π-bonding orbitals reduced from 30° to 17°.[7] No doubt the precise dihedral angle is not exactly 30°, either in the ground state (**1**) or (**3**), or in the transition state, but in the absence of firm knowledge, the picture we use is conveniently simple at this stage in the development of our understanding.

Although both products (**2**) and (**4**) are the result of a formally *anti* S_E2' reaction, the loss of stereocontrol implicit in the formation of mixtures is generally undesirable in synthesis. For many purposes, the nature of the R group is not important (for example, the double bond is usefully oxidised and cleaved to give a carboxylic acid[8]), in which case it is important to know whether a large group R is more effective in locking the conformation (**1**) or in hindering attack on the lower surface of that conformation.

We now report that, with methods in hand for the synthesis of unsymmetrical allylsilanes (**5b**) and (**5c**),[9] we are able to answer this question; the larger R groups, isopropyl and phenyl, lead to stereochemically cleaner reactions in osmylation, epoxidation, and methylenation, three electrophilic reactions for which it is possible to measure the selectivity without needing optically active allylsilanes. We show our results in Scheme 1, where we confirm that osmylation is less selective than the other reactions.

Vedejs and McClure find that the *cis* allylsilane (**12a**) is better behaved, because the conformation corresponding to (**3**) is now much less abundant. Osmylation is normal in giving the diols (**13a**) and (**14a**) in a ratio of 78:22. Again, we have available a method for the synthesis of the *cis* allylsilanes (**12b**) and (**12c**).[10] Using them, we can show that this ratio is improved when the R group is larger than a methyl group, and that all the reactions are now highly stereoselective, as shown in Scheme 1.

We proved the configuration of the diols by stereospecific eliminations of the silyl and hydroxy groups,[3,5] and of the epoxides (which we did not isolate) by stereospecific desilylative opening using fluoride ion.[3,5] In both cases, the allylic alcohol products were recognisable, since they were our starting materials in the synthesis of the allylsilanes (**5**). We have not proved the configuration of the methylenation products. The assignment has been made by reasonable analogy with the epoxidation reactions, which gave closely similar ratios; but the assignments to (**10a**) and (**11a**) are



Scheme 1. *Reagents:* i, OsO_4, pyridine; ii, *m*-chloroperbenzoic acid; Na_2HPO_4, CH_2Cl_2, 0 °C, 2 h; iii, Me_3Al, CH_2I_2, CH_2Cl_2, hexane, 0 °C; room temp., 3 h.

therefore rather tentative. The conditions we used for the methylenation reaction are those of Yamamoto and his co-workers,[11] which give better yields than the Simmons–Smith procedure. In a few cases, we carried out the Simmons–Smith reaction and got very similar stereoselectivities to those reported in Scheme 1.

That ground-state conformation is correlated with the degree of stereoselectivity is supported by our observation that the coupling constants (shown in Scheme 1) between H^1 and H^2 [defined on (**1**)] are significantly higher for those

allylsilanes that show high diastereoselectivity. A high coupling constant is diagnostic of the conformation with H^1 and H^2 antiperiplanar, with a value of 11.37 representing the highest attainable in hydrocarbons.[12] In conclusion, a phenyl group on the chiral centre is a better choice, when stereocontrol is wanted, in the more sterically demanding reactions of allylsilanes with electrophiles. We can expect electrophiles that do not use extensive bridging in the transition state to be more selective for *anti* S_E2' reaction, since attack on C-3 is displaced away from the hindrance of the R group in (**1**).

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