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STEREOCHEMISTRY IN THE HYDROBORATION OF ALLYLSILANES[1]

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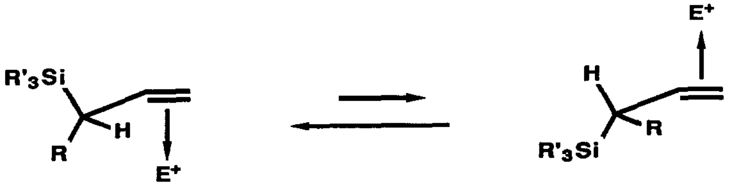
Summary—The hydroboration of allylsilanes is highly stereoselective in the sense (3 → 4 and 6 → 7), especially with 9-BBN as the hydroborating reagent. The products can be converted stereospecifically into 1,3-diol derivatives (5 and 8).

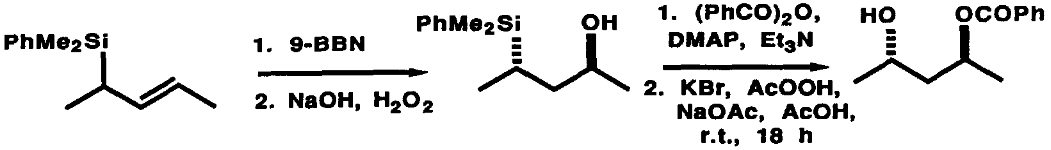
Allylsilanes usually react with electrophiles in the stereochemical sense (1).[2-4] We now report that they generally undergo hydroboration with the same stereochemistry, so that it is



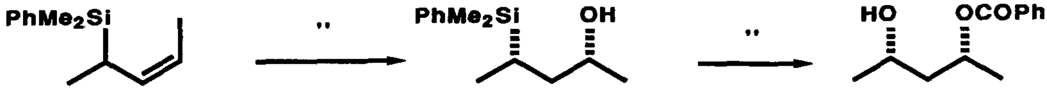
1	2

possible to convert the allylsilanes (3 and 6), first into the γ-silylalcohols (4 and 7), and then into the 1,3-diol derivatives (5 and 8).

We described in the preceding letter how the hydroboration of allylsilanes is regioselective, generally placing the boron atom in a 1,3 relationship to the silyl group,[5] but we did not comment there on the relative stereochemistry for those allylsilanes having both a

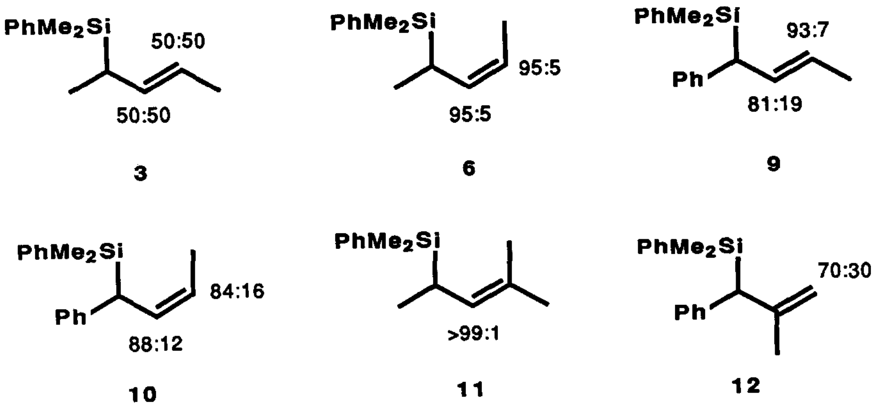


3	4	96%	5	71%

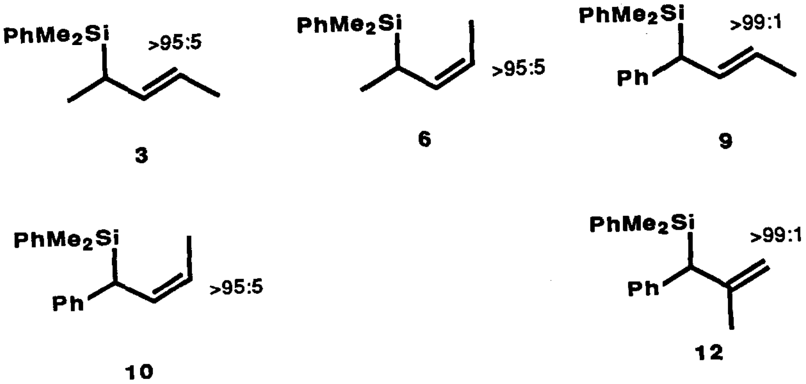


6	7	79%	8	74%

chiral centre at the carbon atom carrying the silyl group and a substituent on the double bond. The structures in Scheme 1 are the allylsilanes from the preceding paper that have these features; the numbers on the structures are the anti:syn ratios for each regioisomer when the hydroborating reagent is the borane:tetrahydrofuran complex. We define attack in the sense (1) as *anti* and the corresponding attack on the upper surface (2) as *syn*, because we believe that 1 is usually both the most populated and the most reactive conformation. In every case but one, hydroboration is mainly *anti* for both regioisomers. The exception is with the allylsilane (3) having a methyl group on the chiral centre and a hydrogen on the double bond *cis* to the chiral centre. The lack of selectivity in this case is not surprising in view of the poor selectivity that this type of allylsilane has already shown in its reactions with osmium tetroxide,[3] peracid,[3] the Yamamoto version of the Simmons-Smith reagent,[4] and in cycloadditions with nitrile oxides.[6] We[4] and Vedejs and McClure[3] have accounted for the poor selectivity in these reactions by invoking the alternative conformation (2), which is only slightly higher in energy, and in which the upper surface is less hindered than the lower surface of 1. In support of this explanation, the corresponding *cis* allylsilane (6), for which conformation (2) is less accessible, is much more selective in these reactions,[7] and



Scheme 1 ***anti*:*syn* Ratios in Hydroboration by BH_3:THF**



Scheme 2 ***anti*:*syn* Ratios in Hydroboration by 9-BBN**

hydroboration is evidently no exception. Having a phenyl group on the chiral centre in place of the methyl group improves the stereoselectivity, as shown by the hydroboration of the allylsilanes (**9**). This is also in agreement with our earlier observations with other electrophiles.[4]

The stereoselectivity with borane:THF, like the regiochemistry described in the preceding letter, is only moderately good. The stereoselectivity is much better, just as the regiochemistry is, when hydroboration is carried out with 9-BBN, the results for which are illustrated in Scheme 2. Surprisingly, the stereochemistry with the allylsilane (**3**) is now highly anti, a fact that does not fit ours and Vedejs's explanation for the poor selectivity that this allylsilane often shows. In that explanation it was the more hindered electrophiles that reacted with allylsilanes in conformation (**2**), because, we argued, the upper surface of **2** is less hindered than the lower surface of **1**. 9-BBN is generally regarded as a more hindered reagent than borane itself,[8] yet it is reacting, apparently, in the general manner (**1**) to a greater extent than borane itself does. Clearly the explanation has to be more complicated than we thought, just as the stereochemistry of Diels-Alder reactions on dienes with a chiral centre adjacent to the conjugated system is more complicated than it was first thought to be.[9]

In each case we oxidised the products of the hydroboration to the corresponding alcohols. We assigned stereochemistry to the β-silylalcohols either by unambiguous synthesis or by Peterson elimination, and we assigned stereochemistry to the γ-silylalcohols, where the products were not already known, by conversion of the phenyldimethylsilyl group into a hydroxy,[10] and comparison of the 1,3-diols so produced with authentic samples. In this way we were able to prepare both 1,3-diol derivatives (**5** and **8**), and, using our new method for converting phenyldimethylsilyl groups to hydroxyls,[11] the 1,2-diol derivative (**14**) and the 1,3-diol derivative (**16**). The hydroboration of allylsilanes is therefore effective for the synthesis of both 1,3- and 1,2-related stereocentres.

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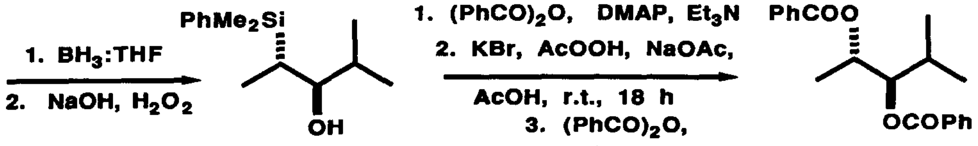
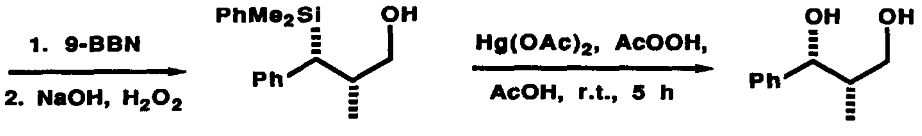


13 >99:1 71%

14 60%

12



15 >99:1 96%

16 70%

Finally, we note the contrast between the stereochemistry of hydroboration of **12** and of a similar compound (**17**) having a hydroxy group in place of the silyl and a n-butyl group in place of the phenyl. With this allyl alcohol, Still and Barrish[12] found selectivity with 9-BBN of 11:1 in favour of the diastereoisomer (**18**), in other words with stereochemistry in the opposite sense to that observed by us. Since the hydroxy group is a π-donor, a σ-acceptor, and not large, and the silyl group is a π-acceptor, a σ-donor, and large, this is perhaps not too surprising.

17 **18** 11:1 80%

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