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INTRAMOLECULAR PROTODESILYLATION OF ALLYL SILANES: 1,3- AND 1,4-ASYMMETRIC INDUCTION

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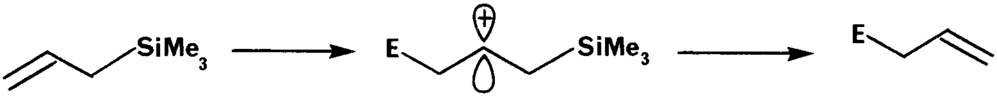
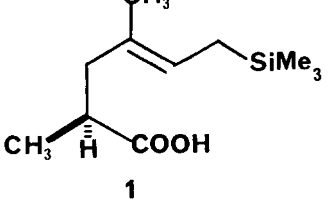
Abstract: Protonation of allylsilanes containing a basic site occurs with intramolecular proton transfer and concomitant remote asymmetric induction.

The protonation of allylsilanes generally occurs[1] on the γ-carbon leading to a silicon stabilized β-cation with subsequent loss of TMS (eq. 1).



(1)

We have recently reported[2] the first example of an intramolecular protonation 1 → 2 which led to 1,3-asymmetric induction with good (>8:1) selectivity. This observation prompted further studies that indicate intramolecular protonation is quite general.



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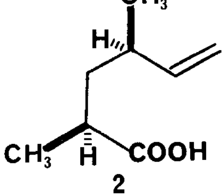

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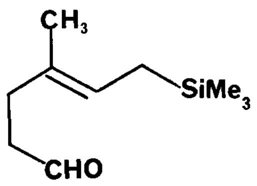
Aldehyde 3[2] reacts with the appropriate alkyl lithiums to produce the alcohol substrates, 4a, 4b, 4c and 4d used in this study.



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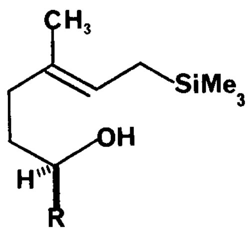
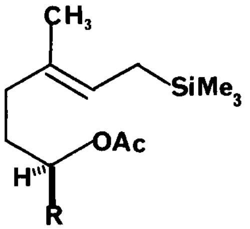
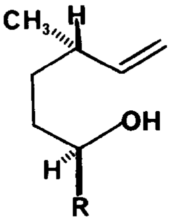


4a. R= CH_3
b. R= *n*-Bu
c. R= *t*-Bu
d. R= $C(CH_3)_2-CH=CH_2$

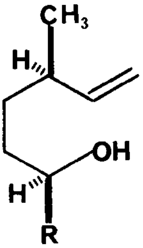


5a. R= CH_3
b. R= *n*-Bu
c. R= *t*-Bu
d. R= $C(CH_3)_2-CH=CH_2$

Acetylation gave 5a,b,c,d (Ac_2O, Et_3N, DMAP, THF, 100%). When 4a,b,c,d was protonated[3] ($BF_3 \cdot AcOH$, CH_2Cl_2), alcohols 6a,b,c,d were formed selectively[4] as well as ether 8[5] (Table entries 1, 2, 3 and 4). If the corresponding acetates 5a,b,c,d were protodesilylated under the same conditions the reverse selectivity is observed! (Table, entries 5, 6, 7 and 8.)



6a. R= CH_3
b. R= *n*-Bu
c. R= *t*-Bu
d. R= $C(CH_3)_2-CH=CH_2$



7a. R= CH_3
b. R= *n*-Bu
c. R= *t*-Bu
d. R= $C(CH_3)_2-CH=CH_2$

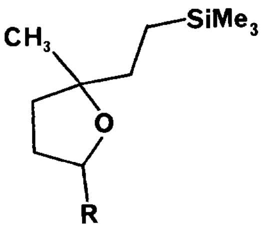


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Table: 1,4-Asymmetric Induction

ENTRY	SUBSTRATE	RATIO 6/7[a]
1	4a	66/34
2	4b	75/25
3	4c	87/13
4	4d	90/10
5	5a	33/67
6	5b	33/67
7	5c	34/66
8	5d	34/66

a. analysed by capillary GC of the acetates

The observed stereochemistry can be explained by intramolecular protonation[6] via a six-membered transition state (fig. 1) for 4a,b,c,d or an eight-membered transition state for 5a,b,c,d (fig. 2). An eight-membered transition state has been suggested[7] to be the most stable for proton transfers, however, the reason for the reversal of stereoselectivity is not obvious. Clearly, much more work must be done to probe the conformational factors controlling the 1,4-asymmetric induction. One feature is evident from the table; the size of group R, is more important for the six-ring proton transfer than for eight.[8]

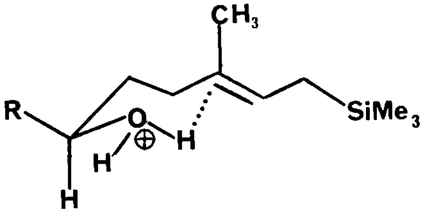


fig 1

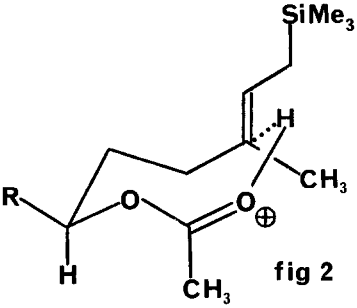


fig 2

We are currently applying this new methodology to problems of acyclic stereoselection. One such example is the synthesis of a key intermediate for Boromycin[9] which is available from 6c. Thus, the methodology is shown to be of value in current problems of acyclic stereocontrol. Studies are continuing.

References and Notes

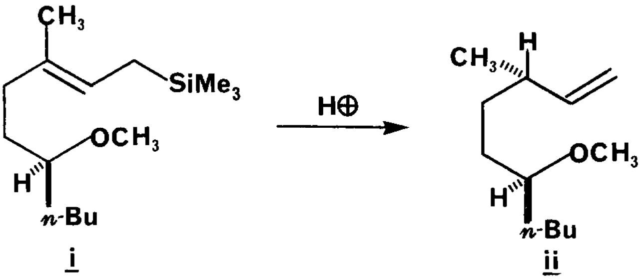
1. Fleming, I.; Marchi, Jr., D.; Patel, S.K.; J.C.S. Perkin I., 1981, 2518-2519.

2. Wilson, S.R.; Price, M.F.; J. Am. Chem. Soc., 1982, 104, 1124-1126.

3. Chan, T.H.; Fleming, I.; Synthesis, 1979, 761-786.

4. The relative configuration of 6 and 7 were proven by ozonolysis and lactonization. While alcohol 1,4-isomers 6/7 could not be separated by glass capillary GC (15M fused silica, carbowax 20M) nor could the carbon resonances be resolved at 25.1 MHz, most carbon signals were doubled at 63 MHz. The corresponding acetates of 6/7, however, could be separated by glass capillary GC.

5. Formation of tetrahydrofuran 8 could be completely surpressed by using the methyl ether i. The 1,4-selectivity was identical but the methyl ethers could not be separated by capillary GC. Thus, the stereochemical study was carried out on the alcohols.



6. a. Intramolecular proton transfers have been the subject of a large body of work: Bell, R.P.; "The Proton in Chemistry," 2nd Ed., Chapman and Hall, London, 1973.

   b. Bernasconi, C.F.; Hibdon, S.A.; McMurry, S.E.; J. Am. Chem. Soc., 1982, 104, 3459-3471.

7. An eight-membered ring transition state has been suggested to be the most favorable for proton transfer: Gandour, R.D.; Tetrahedron Lett., 1974, 295-298.

8. Certain "corner positions" of eight-membered ring conformers have little energy difference between axial and equatorial: cf. Anet, F.A.L.; St. Jacques, M.; J. Amer. Chem. Soc., 1966, 88, 2586-2587.

9. Hanessian, S.; Tyler, P.C.; Demially, G; Chapleur, Y.; J. Amer. Chem. Soc., 1981, 103, 6243-6246.

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