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Epoxidation and Cyclopropanation of 2-Silyl-3-alkenols. A Study of 1,2-Asymmetric Induction.

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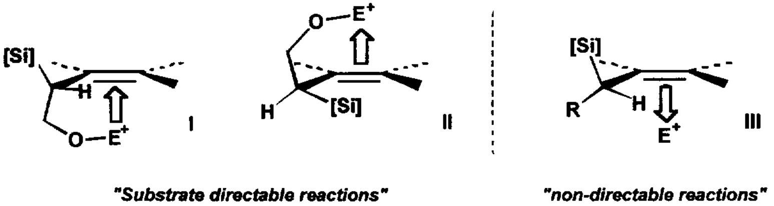
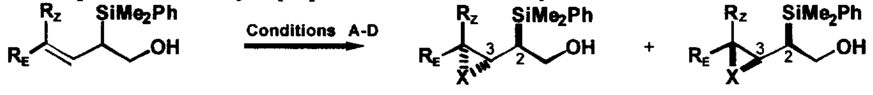
Abstract: Epoxidation and cyclopropanation of 2-silyl-3-alkenols have been shown to occur with high 1,2-stereocontrol through substrate directable reactions. Both *syn* and *anti* epoxides are thus available from *E* and Z-allylsilanes. This contrasts with the results usually observed for allylsilanes lacking a co-ordinating group.

Electrophilic additions to allylsilanes possessing an asymmetric centre adjacent to the double bond are known to proceed with good to excellent stereocontrol.[1] In the course of our studies on α-silylcarbonyl derivatives, we recently reported electrophilic *5-endo-trig* like cyclizations of 2-silyl-3-alkenols which effectively occur with high 1,2-asymmetric induction.[2] Extension of this work to intermolecular electrophilic reactions on this new class of allylsilanes is attractive since it is envisioned that coordination of the incoming electrophile (E^+) by the chelating OH group might be able to direct preferentially the attack on one face of the π-system through conformation I or II (Scheme 1). This *"substrate directable electrophilic reaction"*[3] should thus provide a higher degree of 1,2-stereocontrol than that of non-directed reactions (*i.e.* **III**). We describe here our preliminary investigations on epoxidation and cyclopropanation of various 2-silyl-3-alkenols such as **1** (Scheme 2).



Scheme 1



1 *anti* **2** *syn* **3**

Scheme 2

The epoxidations were carried out using either $Ti(Oi\text{-}Pr)_4$-*t*-BuOOH (A),[3,4a] $VO(acac)_2$-*t*-BuOOH (B)[3,4b,c] or m-CPBA (C),[3,4d] whereas cyclopropanations were performed using the Furukawa procedure (D).[5] **1a-d**[6] smoothly underwent reactions to give the desired products in high yields whatever the conditions (A-D, Scheme 2, Table 1). Interestingly, no Peterson elimination was observed even in the presence of $Zn(Et)_2$ or m-CPBA.[7]

The stereochemistry of the epoxides **2** and **3** (X = O) was assigned unambiguously by using the *anti* stereospecific acid-catalyzed Peterson elimination (Scheme 3). Using this sequence, olefins **4** and **5** were obtained in ratios which corresponded to the ratio of the starting epoxides.[8] The *anti* Peterson elimination finally showed that the *E*- and Z-olefins were formed from the *anti* and *syn* epoxides respectively.[7c] The relative configurations of cyclopropanes **2** (X = CH_2) were determined using a similar sequence.[9]

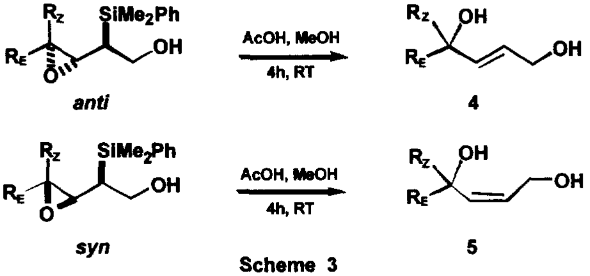
We observed that epoxidations and cyclopropanations of Z-olefins and even of *E*-olefins gave good to excellent diastereoselectivities. Most remarkably, we also found that during ***Ti and V-catalyzed epoxidation, E- and Z-allylsilanes led to opposite face selectivity, affording the syn and anti***

epoxides respectively. This is in sharp contrast to what has previously been observed with closely related analogues lacking a hydroxy group in the vicinity of the allylic asymmetric centre, where both *Z*- and *E*-allylsilanes led to *anti* epoxides.[1c-e,10] This disparity indicates that the OH group is having a profound effect on the transfer of stereochemical information through coordination to the incoming electrophile.[3,10]

Table 1. Epoxidation and cyclopropanation of 2-silyl-3-alkenols **1a-d** (Scheme 2).

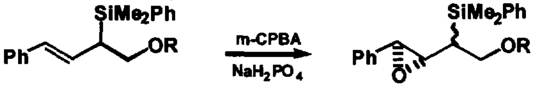
Entry	Substrate	R_Z	R_E	Conditions[a]	Time (h)	X	*anti* **2** / *syn* **3**[b]	Yield[c]
1	**1a**	H	Ph	**A**	24	O	8 : 92	84
2	**1a**	H	Ph	**B**	16	O	15 : 85	85
3	**1a**	H	Ph	**C**	24	O	70 : 30	95
4	**1b**	H	n-C_5H_{11}	**A**	24	O	18 : 82	90
5	**1b**	H	n-C_5H_{11}	**B**	16	O	19 : 81	90
6	**1b**	H	n-C_5H_{11}	**C**	24	O	76 : 24	90
7	**1c**	n-C_5H_{11}	H	**A**	24	O	> 98 : < 2	70
8	**1c**	n-C_5H_{11}	H	**B**	16	O	-	-[d]
9	**1c**	n-C_5H_{11}	H	**C**	24	O	> 98 : < 2	76
10	**1d**	Me	Ph	**A**	24	O	> 98 : < 2	91
11	**1d**	Me	Ph	**B**	16	O	> 98 : < 2	85
12	**1d**	Me	Ph	**C**	24	O	> 98 : < 2	77
13	**1a**	H	Ph	**D**	6	CH_2	93 : 7	88
14	**1b**	H	n-C_5H_{11}	**D**	6	CH_2	> 98 : < 2	83
15	**1c**	n-C_5H_{11}	H	**D**	6	CH_2	> 98 : < 2	71
16	**1d**	Me	Ph	**D**	7	CH_2	> 98 : < 2	79

[a] Conditions : **A** : Ti(O*i*-Pr)$_4$ (1 eq.), *t*-BuOOH (1.5 eq.), CH_2Cl_2, -10°C; **B** : VO(acac)$_2$ (cat.), *t*-BuOOH (1.7 eq.), CH_2Cl_2, 20°C; **C** : *m*-CPBA (2 eq.), K_2HPO_4 (2.7 eq.), CH_2Cl_2, 20°C; **D**: CH_2I_2 (5 eq.), Zn(Et)$_2$, (5 eq.), CH_2Cl_2, RT. [b] Estimated by ^1H NMR (360 and 400 MHz). [c] Crude yields of epoxides estimated using ^1H NMR. Isolated yields of cyclopropane after purification by chromatography. [d] Complex mixture.



Scheme 3

In order to demonstrate the directing ability of the OH function, we repeated the epoxidation and cyclopropanation using the corresponding acetate **6** and silyl ether **7**. As expected, titanium- and vanadium-catalyzed epoxidations gave no reaction whereas cyclopropanation using Zn(Et)$_2$-CH_2I_2 afforded Peterson elimination products. On the other hand, *m*-CPBA produced the epoxides **8** and **9**,[11] in both cases the *anti* isomer

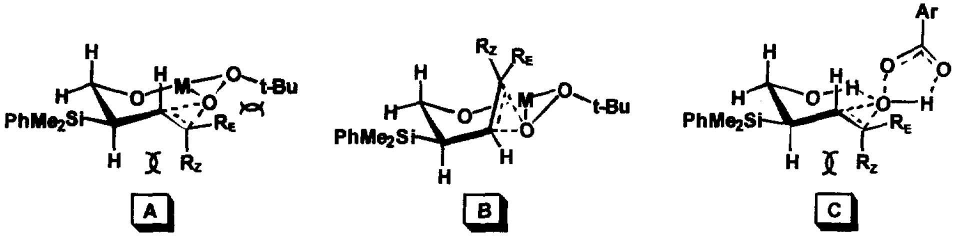


Scheme 4

6, R = Ac
7, R = SiPh$_2$t-Bu
8, R = Ac, *anti/syn* 79:21
9, R = SiPh$_2$t-Bu, *anti/syn* 84:16

being obtained as the major one (Scheme 4). This clearly supports our assumption that the metals Ti, V, or Zn, and their ligands are coordinated to the substrate[3] through the oxygen and are thus very close to the double bond to be functionalized. On the other hand, with m-CPBA, changing the substituent on oxygen did not change the selectivity.[12]

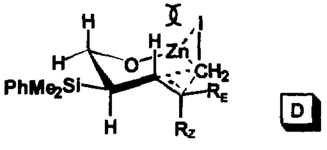
The stereoselectivity of the epoxidations was rationalized using the *"chair-like"* transition states **A**, **B**, or **C** (Scheme 5), depending on the reaction conditions (A-C) (the ligands have been omitted for clarity).[13] The bulky silicon group occupies a pseudoequatorial position to minimize $A_{1,3}$ interactions.[14] With allylsilanes having a *Z*-substituent (**1c-d**), the conformation **A**, where strong Si ↔ R_Z interactions are absent, is preferred (whatever the reagents are), explaining the high selectivity in favour of the *anti*-isomer obtained in such cases (entries 7-12). In contrast, with *E*-allylsilanes under conditions A and B (entries 1,2,4,5), the major *syn*-isomer is formed through a *"chair-like"* transition state **B**, which is more favourable than **A** due to the unfavourable R_E ↔ oxo-complex interactions present in the latter. The opposite topicity for the metal-mediated epoxidation of *E*- and *Z*-allylsilanes **1a-d** would therefore be mainly directed by steric interactions between R_Z and R_E subtituents on the olefin and the ligands on vanadium and titanium.



Scheme 5

By comparison, lower diastereoselectivities with *E*-olefins and formation of the *anti*-isomer with **1a-d** were observed during m-CPBA epoxidations (entries 3,6,9,12). This can be explained by invoking a unique conformation **C** at the transition state independently of the double bond geometry. This suggests that in contrast to the metal-catalyzed reactions, m-CPBA induces little steric interactions. It also supports our hypothesis that the size of the metal and its ligands influence the facial selectivity of the epoxidation through steric interactions with the R_Z and R_E substituents, a feature which does not exist in the case of co-ordination through hydrogen-bonding (*i.e.* **C**).

Similarly, Simmons-Smith cyclopropanations gave the *anti* cyclopropylmethylsilanes **2** ($X=CH_2$) as sole products, irrespective of the geometry of the starting olefin. A *"chair-like"* transition state such as **D** was therefore envisioned (Scheme 6). Steric hindrance around the iodine atom on the metal probably prevents the cyclopropanation of *E*-olefin if it were to proceed through a conformation similar to **B**, explaining the absence of *syn* products in this reaction. Therefore, as before, the steric interactions between R_Z and R_E and the ligands on zinc (including iodine) control the diastereofacial selectivity of the cyclopropanation.



Scheme 6

In summary, we have reported highly stereoselective epoxidations and cyclopropanations of a new type of allylsilanes. We showed that in sharp contrast with what has been reported previously,[1a-e,12] *anti* and *syn* epoxides **2** and **3** are both available via directed epoxidation of the corresponding *Z*- and *E*-allylsilanes. We also found that in contrast to epoxidation, cyclopropanation led to the same diastereoisomer irrespective of the double bond geometry. It appears that the stereocontrol is mainly directed by strong steric interactions between the substitutents R_Z and R_E of the olefin and the metal complex as indicated by the lower stereoselectivity obtained with m-CPBA. Further studies directed towards the utilization of these new synthons in organic synthesis are now underway in our laboratory.

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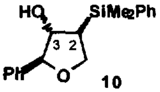
References and Notes

1. (a) Fleming, I. *Pure & Appl. Chem.*, **1988**, *60*, 71-78 and references cited therein; (b) Fleming, I., *Pure &*

Appl. Chem., **1990**, *62*, 1879-1886; (c) Fleming, I. *J. Chem. Soc., Perkin Trans 1*, **1992**, 3363-3369; (d) Fleming, I.; Lawrence, N.J.; Sarkar, A.K.; Thomas, A.P. *J. Chem. Soc., Perkin Trans 1*, **1992**, 3303-3308; (e) Fleming, I.; Lawrence, N.J. *J. Chem. Soc., Perkin Trans 1*, **1992**, 3309-3326; (f) Murphy, P.J.; Russell, A.T.; Procter, G. *Tetrahedron Lett.*, **1990**, *31*, 1055-1058; (g) Ward, A.; Procter, G. *Tetrahedron Lett.*, **1992**, *33*, 3363-3366; (h) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.*, **1989**, *37*, 57-575.

2. Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron Lett.*, **1995**, *36*, 2987-2990.
3. For an excellent review on substrate-directable reactions, see : Hoveyda, A.H.; Evans, D.A.; Fu, G.C. *Chem. Rev.*, **1993**, *93*, 1307-1370 and references cited therein.
4. (a) Martin, V.S.; Woodard, S.S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K.B. *J. Am. Chem. Soc.*, **1981**, *103*, 6237-6240; (b) Sharpless, K.B.; Verhoeven, T.R. *Aldrichimica Acta*, **1979**, *12*, 63-74; (c) Rossiter, B.E.; Verhoeven, T.R.; Sharpless, K.B. *Tetrahedron Lett.*, **1979**, 4733-4736; (d) Johnson, M.R.; Kishi, Y. *Tetrahedron Lett.*, **1979**, 4337-4350.
5. (a) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron Lett.*, **1966**, 3353-3354; (b) Nishimura, J.; Kawabata, N.; Furukawa, J. *Tetrahedron*, **1969**, *25*, 2647-2569. For recent reports, see : (c) Morikawa, T.; Sasaki, H.; Hanai, R.; Shibuya, A.; Taguchi, T. *J. Org. Chem.*, **1994**, *59*, 97-103; (d) Mohr, P. *Tetrahedron Lett.*, **1995**, *36*, 7221-7224; (e) Charette, A.B.; Lebel, H. *J. Org. Chem.*, **1995**, *60*, 2966-2967; (f) Lautens, M.; Delanhe, P.H.M. *J. Org. Chem.*, **1995**, *60*, 2474-2487.
6. Landais, Y.; Planchenault, D.; Weber, V. *Tetrahedron Lett.*, **1994**, *35*, 9549-9552.
7. (a) Roush, W.R.; Grover, P.T.; Lin, X. *Tetrahedron Lett.*, **1990**, *31*, 7563-7566; (b) Roush, W.R.; Grover, P.T. *Tetrahedron Lett.*, **1990**, *31*, 7567-7570; (c) Roush, W.R.; Grover, P.T. *Tetrahedron*, **1992**, *48*, 1981-1998.
8. Acidic treatment of the mixture of epoxides **2a** and **3a** (R_E=Ph, X=O), afforded a mixture of the expected olefin (**4a**), along with a tetrahydrofuran **10** having the stereochemistry depicted in Fig.1. This results from the opening of the epoxide followed by a stereoselective *5-endo-trig* cyclization. It should be emphasized that **10** is formed from epoxide **3a**, reflecting the stereochemistry of the starting epoxide since C-2 and C-3 centres are left unchanged during the cyclization[9] (Scheme 2 and Fig.-1).



10

Fig.-1

9. Landais, Y.; Parra-Rapado, L. *Tetrahedron Lett.*, following communication in this issue.
10. Panek, J.S.; Garbaccio, R.M.; Jain, N.F. *Tetrahedron Lett.*, **1994**, *35*, 6453-6456.
11. The stereochemistry of **8** and **9** was determined as described for epoxides **2** and **3**.
12. Formation of the *anti* epoxides **8** and **9** can be rationalized by invoking either a directed or a non-directed epoxidation mechanism.[1,3]
13. Mihelich, E.D.; Daniels, K.; Eickhoff, D.J. *J. Am. Chem. Soc.*, **1981**, *103*, 7690-7692.
14. Hoffmann, R.W. *Chem. Rev.*, **1989**, *89*, 1841-1860.

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