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# Asymmetric allylation of aldehydes and glyoxylates through 'C-centered' chiral pentacoordinate allylsilicates or promoted by Lewis acid[1]

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**Abstract**

One-pot asymmetric allylation of aldehydes and glyoxylates with 'C-centered' chiral pentacoordinate allylsilicates generated from a chiral diol-modified allyltrichlorosilane **8** in the presence of Lewis bases, gave optically active homoallylic alcohols **4** with relatively high enantioselectivity (up to 81% ee). The reactions proceed via a six-membered cyclic transition state. In contrast, the allylation reactions of glyoxylate with allylalkoxysilanes promoted by $TiCl_4$ proceed through an acyclic transition state. The chiral auxiliaries residing at different positions on the molecules exhibited different abilities for asymmetric induction, depending on the reaction pathway and the stereochemistry of the transition state. 

## 1. Introduction

The allylation of carbonyl compounds with allylsilanes under Lewis acid conditions, first described by Hosomi and Sakurai,[2] has been extensively used in synthesis for the formation of C–C bonds (Scheme 1).[3] The possibility of using this reaction for the asymmetric synthesis of optically active homoallylic alcohols, which can be converted to many important building blocks for optically active natural product synthesis, has attracted considerable attention.[4] Recently, it has been found that the substituents on silicon can offer stereocontrol in the reaction, even though the reaction center is remote from the silicon atom.[5] However, for the reaction of aldehydes with both 'Si-centered' (chirality on silicon) and 'C-centered' (chirality on the carbon of one of the substituents) chiral allylsilanes, only modest enantioselectivity has been observed.[4] This was attributed to the reaction (under Lewis acid conditions) proceeding through a less rigid, open transition structure (acyclic transition state). It was hoped that if the reaction could be made to proceed through a rigid cyclic transition state, higher asymmetric induction could be obtained. Sakurai[6] demonstrated that allylation of aldehydes with hydroxy

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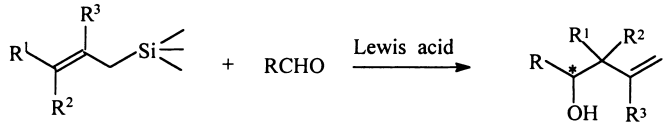
compounds and allyltrifluorosilane in the presence of triethylamine, without a Lewis acid promoter, gave the corresponding homoallylic alcohols in a stereospecific manner. Pentacoordinate allylsilicate intermediates, which have been proved to have Lewis acid characters, were considered as possible promoters.[7] The reaction of pentacoordinate allylsilicate with carbonyl compounds was suggested to proceed through a cyclic transition state. On the other hand, Kobayashi[8] reported that allyltrichlorosilane could also react with aldehydes in DMF or some co-solvent mixture via a pentacoordinate silicate intermediate and six-membered cyclic transition state. Recently, chiral Lewis bases were employed to catalyze asymmetric allylation, improving the enantioselectivity (65–92% ee).[9,10] Herein, we wish to report the investigation on the asymmetric allylation of aldehydes and glyoxylates via 'C-centered' chiral pentacoordinate allylsilicates generated from chiral alcohol-modified allyltrichlorosilane in the presence of Lewis bases.[11] It is also interesting to examine the pathway of the reaction of glyoxylates with chiral allylalkoxysilanes under Lewis acid conditions, which should be through a Lewis acid coordinated intermediate. Comparing pentacoordinate silicate intermediates with Lewis acid coordinated intermediates, two different reaction pathways and related stereochemistry could be described. It is helpful to understand the roles of the chiral auxiliaries resident on different parts of the molecule for asymmetric induction in the allylation reactions.



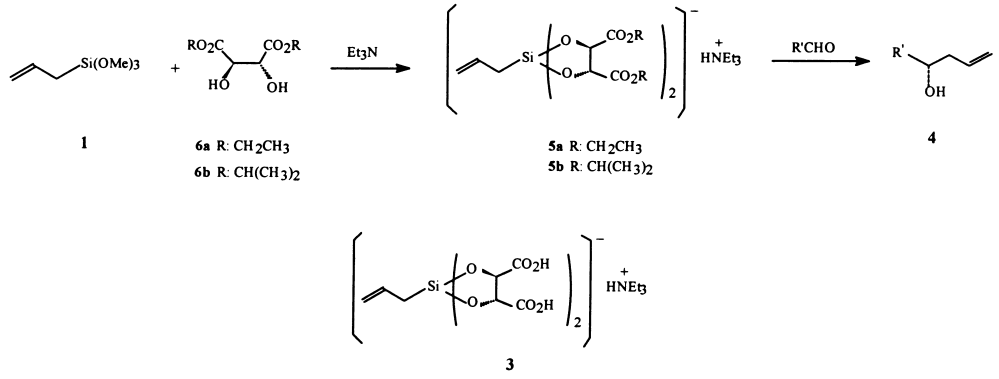

Scheme 1.

## 2. Results and discussion

### *2.1. Allylation through a pentacoordinate allylsilicate intermediate*

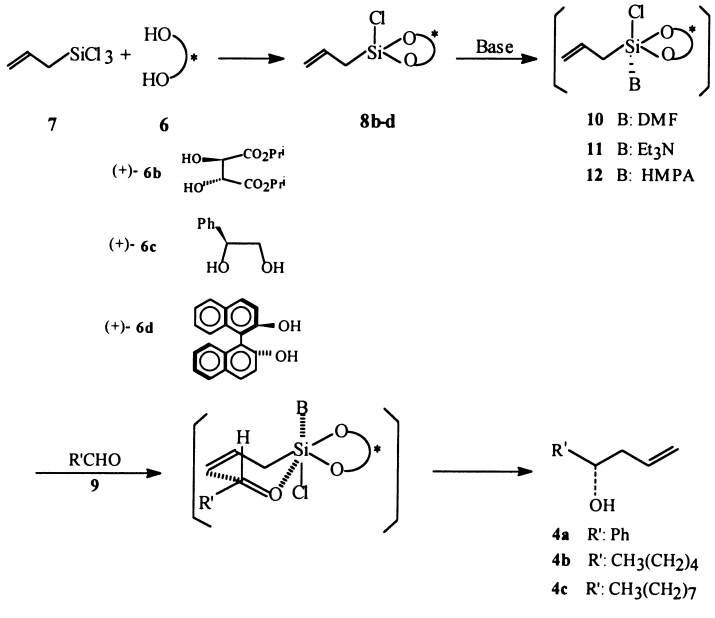
Several groups have described the reaction of pentacoordinate allylsilicates with carbonyl compounds,[7] but very few reported the asymmetric reaction using 'C-centered' chiral pentacoordinate allylsilicate. As Hosomi suggested,[12] from a 1:2 mixture of allyltrimethoxysilane **1** and (+)-tartaric acid **2**, a 'C-centered' chiral pentacoordinate silicate intermediate **3** was generated in situ, which subsequently reacted with aldehydes to offer chiral homoallylic alcohols **4** with low enantioselectivity (10–17% ee). For comparison, we prepared optically active pentacoordinate silicates, (+)-triethylammonium bis[(*R*,*R*)-tartrato(2-)]silicates [(+)-**5a**–**b**], from **1** and (+)-(2*R*,3*R*)-tartrates (**6a**–**b**), in 55 to 68% yield (Scheme 2). By using optically active pentacoordinate silicates **5a**–**b**, the asymmetric allylation of either aromatic or aliphatic aldehydes was carried out without a catalyst to give optically active homoallylic alcohols **4** with 7–25% ee. It is suggested that a 'chiral dilution effect'[13] caused by bis-chiral auxiliaries on one silicon atom was responsible for the poor enantioselectivity.

Although attempts to prepare 'C-centered' mono-chirally substituted pentacoordinate allylsilicates have not been successful, we are still interested in generating them in situ. As mentioned above, allyltrichlorosilane **7** can react with aldehydes in the presence of Lewis bases without a catalyst, giving homoallylic alcohols. We hoped that by using a chiral diol to modify **7** in the Kobayashi reaction system,[8] and thus generating in situ a 'C-centered' mono-chirally substituted pentacoordinate allylsilicate, the enantioselectivity of the subsequent asymmetric allylation could be improved. (+)-Diisopropyl tartrate, (+)-**6b**, was treated with **7** in dichloromethane for 3 h at room temperature and then the mixture was concentrated to generate crude product **8b**. Based on the known reaction of dichlorodimethylsilane with




Scheme 2.

a tartrate species to give a cyclic silane,[14] **8b** should be a cyclic species. A one-pot procedure for the subsequent allylation reaction in the presence of Lewis base has been recommended.[8,9] If a small quantity of **7** remained in the crude product **8b**, it might participate in the subsequent reaction with the aldehyde, thus reducing the enantioselectivity. Therefore, (+)-**6b** was used in a slight excess. Prolonging the reaction time ensured that the formation of cyclic **8b** proceeded completely. In order to avoid the formation of a bis-chirally substituted pentacoordinate allylsilicate **5**, for **6b** and **7**, parallel addition of two reagents must be employed and the addition speed of the starting materials must be strictly controlled. Moreover, it was important not to use a base to absorb HCl produced in the course of the reaction. Without further purification, the reactions of **8b** with aldehyde **9a–c** were carried out in the presence of Lewis bases, such as $Et_3N$, DMF and HMPA, giving the corresponding optically active homoallylic alcohols **4a–c**[15–17] in a reasonable overall yield (Scheme 3). Chiral diols, (+)-1-phenylethanediol **6c** and (+)-2-binaphthol **6d**, were also selected as modifiers, which could react with **7** to produce the corresponding cyclic silanes **8c** and **8d** under the same conditions and be applied in the allylation of aldehydes.




Scheme 3.

The $^{29}Si$ NMR spectrum of **8b** showed only one upfield peak at δ −170.3 ppm in DMF, while a

downfield peak at δ 1.96 ppm was observed in $CDCl_3$. This provides evidence for the formation of a pentacoordinate silicate intermediate **10** in the solution of **8b** in DMF. On the other hand, there was no **7** present in the crude product **8b** ($^{29}$Si NMR of **7**, δ 8.0 ppm in $CDCl_3$).[8b] Apparently, a molecule of DMF, which plays the role of a Lewis base, participates in the coordination of the silicon atom of **8b**, generating a chiral pentacoordinate silicate **10**. Similarly, since $Et_3N$ and HMPA also have the ability to coordinate with the silicon atom, chiral pentacoordinate silicates **11** and **12** can also be considered as intermediates in the reaction. The chiral pentacoordinate silicates **10**–**12** are of sufficient Lewis acidity to undergo nucleophilic addition to aldehydes, giving the optically active homoallylic alcohols **4a**–**c**. All three bases can promote the allylation reaction, but exhibit different promoting ability, the best for $Et_3N$ and the worse for HMPA. As shown in Table 1, the enantioselectivities of the products **4** were as high as 81%. The ees of the reactions promoted by DMF were better than those promoted by $Et_3N$. However, in the case of DMF, although the reactions proceeded smoothly, the yield was relatively low. Lower reaction temperatures were found to enhance the ee slightly. Compared with the reaction of aromatic aldehydes, aliphatic aldehydes reacted sluggishly but with higher ee. Among the selected chiral diols (**6b**–**d**), the ability of a tartrate moiety (**6b**) for asymmetric induction is much larger. In the case of 2-binaphthol **6d**, the reaction was slowed down markedly, probably due to the steric effect. Despite strong reaction conditions being employed (refluxing in chloroform for 48 h), the yield of the homoallylic alcohol **4a** was only 14% with 29% ee. It is interesting to compare the above with the reactions of 'C-centered' chiral allylalkoxysilane with aldehydes promoted by a Lewis acid (~20% ee), which are suggested to proceed through acyclic transition states.[18] However, the reaction of a chiral diol-modified allyltrichlorosilane **8**, an analogue of a 'C-centered' chiral allylalkoxysilane, with aldehydes in the presence of Lewis bases gave higher enantioselectivity (up to 81% ee). This is due to the reaction proceeding through a pentacoordinate silicate intermediate and subsequently a more rigid six-membered cyclic transition state (see later).

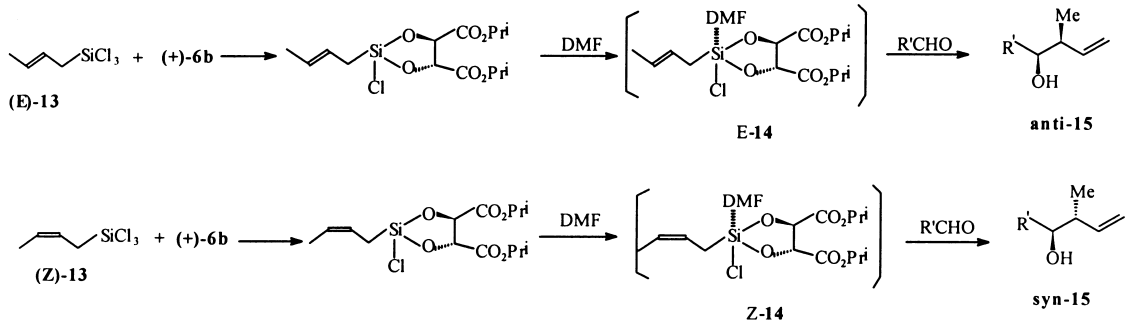
In order to obtain more stereochemical information on the transition state of the reaction of aldehydes with 'C-centered' chiral pentacoordinated allylsilicates, we carried out crotylations of benzaldehyde with chiral pentacoordinate **14** generated in situ from (+)-**6b** and crotyltrichlorosilanes, (*E*)-[19] and (*Z*)-**13**,[20] in the presence of DMF (Scheme 4). The results showed that when (*E*)-**13** (*E*:*Z*=4:1) was used, the product was mainly *anti*-**15**[8b] (*anti*:*syn*=4:1, yield: 72%), while for (*Z*)-**13**, *syn*-**15**[8b] was obtained exclusively (yield 76%). The sense of internal stereoinduction [(*E*)-**13** to *anti*-**15**, (*Z*)-**13** to *syn*-**15**] clearly supports reaction via a hexacoordinate silicon species and a six-membered cyclic transition state. The absolute configuration of the newly created stereogenic center in the homoallylic alcohols **4a**–**c** produced was deduced by comparison with the literature rotation (Table 1). The (*R*)-configurations of aliphatic **4b** and **4c** and (*S*)-configurations of aromatic **4a** are consistent with the stereochemical outcome of the proposed cyclic hexacoordinate silicon species having a chair conformation.

It is worthy to examine which chiral moieties in either chiral substrate or chiral pentacoordinate silicate, mainly contribute to asymmetric induction in the double asymmetric allylation of chiral α-ester aldehydes, with (+)-**8b** in the presence of DMF (Scheme 5 and Table 2). It was observed that only the aldehyde carbonyl group in the molecule of an α-ester aldehyde, (1*R*,2*S*,3*R*)-(−)-menthyl glyoxylate [(−)-**16**][21] is reactive to the pentacoordinate allylsilicate, giving the α-homoallylic hydroxy ester, menthyl 2-hydroxy-4-pentenoate **17**, in yields of 83–87%. There are two doublets at δ 0.78 and 0.82 ppm in the $^1$H NMR spectrum of product **17**, which are assigned to the 10′-H of the menthyl group of the two diastereomers. Thus, the diastereomeric excess (de) of **17** can be determined as 33–38%. The configuration of the newly created stereogenic center was deduced as *S* [cf. Chen et al.[22]]. If (−)-**8b** was used in the reaction with (−)-**16** instead of (+)-**8b**, the de of product **17** decreased to 13% and the configuration of the new chiral center changed to *R*. If one chiral compound in this bis-chiral reactant system, either chiral glyoxylate substrate or chiral silicon reagent, was replaced by an achiral analogue,

Table 1
Asymmetric allylation of aldehydes **9** with diol-modified **7** under Lewis base

| Entry[a] | Aldehyde **9**, $^1$R | Chiral diol | Product | **7** : **6** : **9** | Solvent[b] | Yield[c] % | $[\alpha]_D$ (c,solv.) | Ee[d] % | Confg.[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Ph | (+)-**6b** | **4a** | 3 : 3 : 2 | A | 72 | -12.6(4.4,PhH) | 27 | S |
| 2 | pentyl | (+)-**6b** | **4b** | 3 : 3 : 2 | A | 55 | +3.6(0.9,$CHCl_3$) | (46)[e] | R |
| 3 | octyl | (+)-**6b** | **4c** | 3 : 3 : 2 | A | 69 | +4.7(2.0,$CCl_4$) | 44 | R |
| 4 | Ph | (+)-**6b** | **4a** | 3 : 3 : 2 | B | 50 | -14.9(2.4,PhH) | 32 | S |
| 5 | Ph | (+)-**6b** | **4a** | 3 : 3.3 : 2 | B | 47 | -18.0(4.8,PhH) | 39 | S |
| 6 | Ph | (+)-**6b** | **4a** | 3 : 3.3 : 2 | B | 46 | -24.5(2.3,PhH) | 52 | S |
| 7 | octyl | (+)-**6b** | **4c** | 3 : 3.3 : 2 | B | 47 | +6.6(4.5,$CCl_4$) | 61 | R |
| 8 | octyl | (+)-**6b** | **4c** | 3 : 3.3 : 2 | B | 50 | +7.6(4.4, $CCl_4$) | 71(68)[e] | R |
| 9 | pentyl | (+)-**6b** | **4b** | 3 : 3.3 : 2 | B | 48 | +4.3(2.3,$CHCl_3$) | 55 | R |
| 10 | pentyl | (+)-**6b** | **4b** | 3 : 3.3 : 2 | B | 52 | +6.2(0.5, $CHCl_3$) | 81 | R |
| 11 | Ph | (+)-**6c** | **4a** | 3 : 3.3 : 2 | A | 26 | +4.1(1.7, PhH) | 9 | R |
| 12 | Ph | (+)-**6d** | **4a** | 3 : 3.3 : 2 | A | 14 | +13.3(0.4, PhH) | 29 | R |
| 13 | Ph | (+)-**6b** | **4a** | 3 : 3.3 : 2 | C | 38 | -9.7(3.0, PhH) | 21 | S |
| 14 | octyl | (+)-**6b** | **4c** | 3 : 3.3 : 2 | C | 34 | +1.6(5.8, Ccl4) | 15 | R |

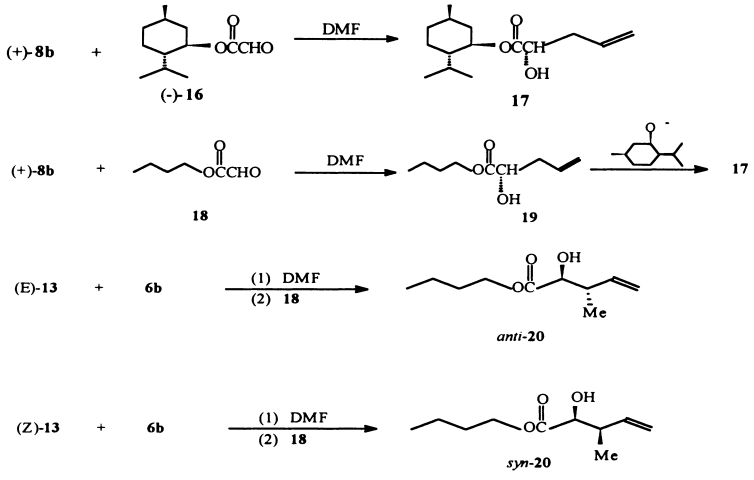
a) reaction conditions: room temp. for 24h (-10°C , 36h for entry 8 and 10; 5°C, 24h for entry 6);
b) co-solvent systerm:A, $Et_3N$(3 equiv.)-$CH_2Cl_2$; B, DMF-$CH_2Cl_2$(1:1);.C, HMPA-$CH_2Cl_2$(1:1); c) isolated yield; d) assigned by comparison with literature rotation values; e) determined by $^1$HNMR (300MHz ) analysis of the MTPA ester.




Scheme 4.

the effect of the chiral auxiliary on stereochemical outcome of the reaction would be more clear. For the reaction of achiral **7** and chiral (−)-**16**, only a 5% de of product **17** was observed. In contrast, the optically active product, (−)-butyl 2-hydroxy-4-pentenoate **19**, produced from allylation of achiral butyl glyoxylate **18** with (+)-**6b** in DMF had 41% de with *S*-configuration, which can be determined by treating with lithium (−)-menthoxide, leading to ester-exchange completely, to give the known compound **17** (Scheme 5). These results indicate that the asymmetric induction is mainly from the chiral auxiliary on the silicon atom, while the chiral moiety on the glyoxylate has little effect on the stereocontrol of the reaction. The crotylation reaction of butyl glyoxylate **18** with (*E*)- and (*Z*)-**13** modified by diol **6b** in the presence of DMF was investigated, (*E*)-**13** was transformed to *anti*-**20**[23] (*anti*:*syn*=5:1, yield: 87%) and (*Z*)-**13** to *syn*-**20**[23] exclusively (yield: 86%), which also provides evidence for reaction via a hexacoordinate silicon six-membered cyclic species with a chair conformation (Scheme 5). In the transition state, the chiral menthoxy group of the glyoxylate is remote to the reaction center providing

very weak asymmetric induction, while the chiral tartrate moiety is close to the six-membered ring, resulting in better asymmetric induction.




Scheme 5.

## 2.2. Allylation of glyoxylate promoted by $TiCl_4$

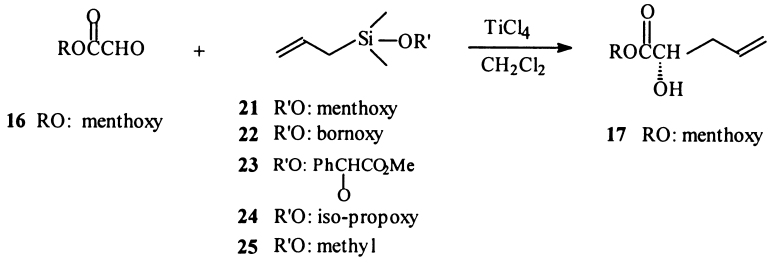
In the past decades, a lot of work has focused on Lewis acid promoted reaction of aldehydes with allylsilanes. For comparison, we carried out the reactions of allylalkoxydimethylsilane **21**–**25**[18] with glyoxylate (−)-**16** in the presence of $TiCl_4$ to obtain more information about the stereochemistry of the reaction (Scheme 6 and Table 3). From the work of Kumada[24] and Fleming,[25] it has been concluded that the Sakurai–Hosomi reaction proceeds through an acyclic antiperiplanar transition state **26**. Denmark[26] suggested that the synclinal transition state **27** is also operative under certain conditions, for example, in intramolecular reactions. Obviously, in a synclinal transition state the silyl group may have a greater effect on the stereochemistry of the reaction. As in our previous work,[18] the chiral alkoxysilyl group could bind with the Lewis acid, which may induce the reaction to proceed through synclinal transition state **28**,[18,27] resulting in asymmetric induction in the course of reaction. However, it is surprising to note that any change in alkoxy substituents on silicon, either chiral allylalkoxydimethylsilanes as **21**–**23** or achiral as allylisopropoxydimethylsilane **24** and allyltrimethylsilane **25**, did not effect the de of the product **17** to any significant extent. Moreover, if either (−)-**21** or (+)-**21** with different configuration, as well as racemic (±)-**23**, were used as a reactant in the reaction with (−)-**16**, all the product **17** had *S*-

Table 2
Asymmetric allylation of glyoxylate **16** and **18** with **8** under DMF[a]

| Entry | Silane | Glyoxylate | Reac. Temp. (°C) | Product | Yield[b] (%) | De (%) |
|---|---|---|---|---|---|---|
| 1 | (+)-**8b** | (-)-**16** | -20 | **17** | 84 | 33(S) |
| 2 | (+)-**8b** | (-)-**16** | -60 | **17** | 85 | 38(S) |
| 3 | (-)-**8b** | (-)-**16** | -60 | **17** | 83 | 13(R) |
| 4 | (+)-**8b** | **18** | -20 | **19** | 83 | 41(S) |
| 5 | **7** | (-)-**16** | -20 | **17** | 86 | 5(S) |

a) all reactions for 12 h at given temperature; b) isolated yield.

configuration (Table 3). In contrast to the results from the reaction via pentacoordinate allylsilicates, the chiral moiety on the glyoxylate plays the main role in asymmetric induction in the Lewis acid promoted allylation reaction. This was attributed to their different reaction pathways and transition states.




Scheme 6.

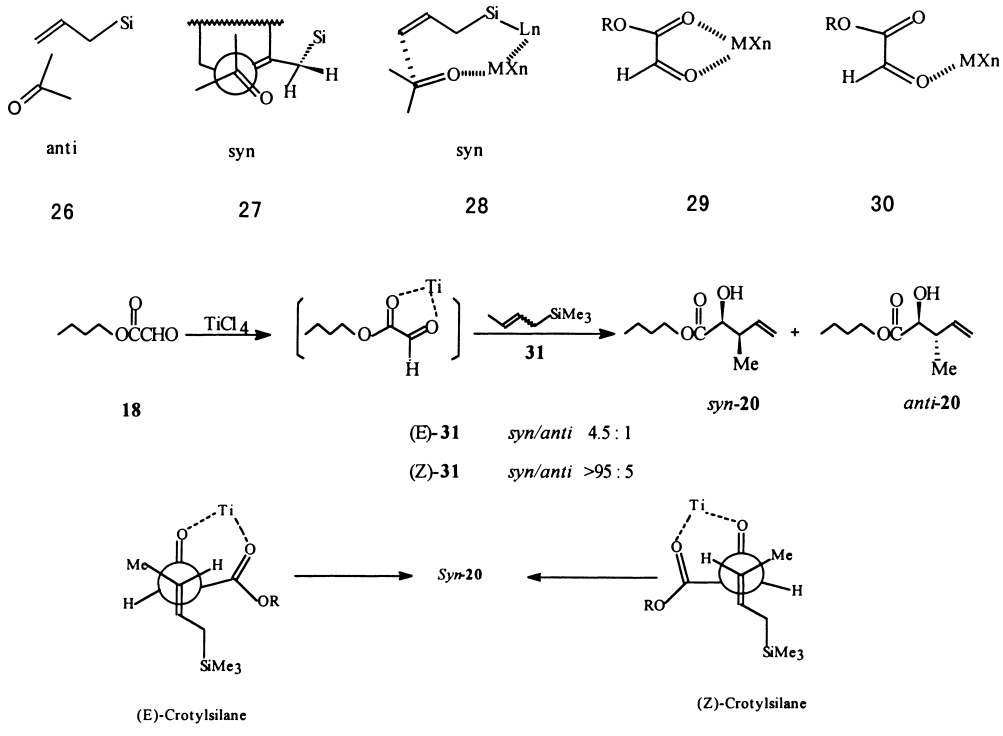
It is also interesting that the addition order of the reagents could influence the de of the product **17** (Table 3). Table 3 shows that if (−)-**16** was first mixed with $TiCl_4$, followed by addition of allylsilanes (method A), the reaction gave a higher de (30–42%). The formation of the chelate complex **29** was assumed, leading to better stereochemical outcome. Nevertheless, if the addition order was changed to first mixing **16** with allylsilane, then adding $TiCl_4$ (method B), the de decreased to 11–14%. This is presumably due to the formation of the mono-complex **30**, but not the chelate complex **29**, and subsequent reaction with silane immediately. Apparently, the stereocontrol from the mono-complex is weaker than that from the chelate complex. At the same time, we tried the crotylation of butyl glyoxylate **18** with crotyltrimethylsilane **31** promoted by $TiCl_4$ with the addition order as method A (Scheme 7). The transformation of (*E*)-**31**[20] (*E*:*Z*=4:1) to *syn*-**20** (*syn*:*anti*=4.5:1, yield: 91%) and (*Z*)-**31**[20] to *syn*-**20** (*syn*:*anti*=>95:5, yield: 87%), respectively, provided an understanding of the stereochemistry of the transition state, in which the carbonyl groups chelated complex with $TiCl_4$ was formed. Hence, there is no longer a coordinate site on Ti atom available to bind silylalkoxy group, thus an open antiperiplanar arrangement of the alkoxysilyl groups could be accomplished. It is reasonable that *syn*-

Table 3
Allylation of (−)-**16** with allylalkoxysilanes **21**–**25** promoted by $TiC_4$[a]

| Entry | Allylalkoxysilane RO | Addition order[b] | Yield of **17** (%)[c] | De (%)[d] |
|---|---|---|---|---|
| 1 | (-)-**21**, menthoxy | method A | 92 | 40 |
| 2 | (+)-**21**, menthoxy | method A | 98 | 36 |
| 3 | (+)-**21** | method B | 87 | 12 |
| 4 | (+)-**22**, bornoxy | method A | 85 | 30 |
| 5 | (+)-**23**, PhCH(O)$CO_2$Me | method A | 87 | 37 |
| 6 | (±)-**23**, PhCH(O)$CO_2$Me | method A | 84 | 38 |
| 7 | **24**, isopropoxy | method A | 90 | 42 |
| 8 | **24** | method B | 92 | 14 |
| 9 | **25**[e] | method A | 90 | 30 |
| 10 | **25** | method B | 85 | 11 |

a) reaction conditions: -78°C for 4h in $CH_2Cl_2$;
b)method A: **16**+$TiCl_4$+silane, method B: **16**+silane+$TiCl_4$; c) isolated yield;
d) configurations of all product **17** are S; e) allyltrimethylsilane.

selectivity is favorable for both (*E*)- and (*Z*)-crotylsilane in the reaction with glyoxylate promoted by $TiCl_4$ (Scheme 7).




Scheme 7.

In summary, the Lewis acid promoted allylation reaction of glyoxylate may proceed through two steps. Firstly, Lewis acid coordinates to both aldehyde and ester carbonyl groups to form a chelate complex, activating them at the same time. Secondly, the allylsilane selectively attacks the *Si* face of the aldehyde carbonyl group, controlled by the chiral auxiliary of glyoxylate to provide the *S*-configuration of the newly formed stereogenic center in the reaction. The alkoxy group is disposed *anti* to the carbonyl groups chelated with $TiCl_4$ (Scheme 7). The chirality of the alkoxysilyl moiety does not bring about the asymmetric induction in the course of the reactions at all.

## 3. Conclusion

One-pot allylation reactions of aldehydes and glyoxylates via a 'C-centered' chiral pentacoordinate allylsilicate intermediate generated in situ from chiral alcohol-modified allyltrichlorosilane **8** in the presence of Lewis bases gives optically active homoallylic alcohols **4** with relatively high enantioselectivities (up to 81% ee). It was confirmed that the reactions proceed through a hexacoordinate six-membered cyclic transition state. The chiral tartrate moiety is close to the six-membered ring of the transition state, resulting in stronger asymmetric induction. In contrast, the allylation reactions of the glyoxylate with allylsilanes promoted by $TiCl_4$ proceed through an acyclic transition state, in which the alkoxy group on silicon is disposed *anti* to the carbonyl groups chelated with $TiCl_4$. The chirality of ester moiety of glyoxylate plays the main role in the asymmetric induction in the course of the reaction.

## 4. Experimental

Melting points were measured on a NAGEMA PHMK 05 apparatus and were uncorrected. IR spectra were recorded on a Perkin–Elmer 782 infrared spectrometer. $^{1}H$, $^{13}C$ and $^{29}Si$ NMR spectra were measured on Varian XL-200 and XL-300 spectrometers with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on an MS-50/PS30 spectrometer. Optical rotations were measured on a Perkin–Elmer 241 spectrometer at 589 nm. Flash chromatography was performed on a silica gel column. All chemicals were reagent grade and used without further purification. The solvents were treated for use in anhydrous reaction conditions before being employed.

### *4.1. General procedure for preparation of pentacoordinate allylsilicates **5a–b***

A solution of allyltriethoxysilane (**1b**) (0.96 g, 6.0 mmol) and (+)-**6b** (2.8 g, 12.0 mmol) in 30 mL of triethylamine was refluxed for 2 h and then cooled to room temperature. The resulting precipitate was filtered and washed with hexane, then dried under vacuum to give a white solid **5b**, 2.1 g (yield 55%).

#### *4.1.1. Triethylammonium bis[(*R,R*)-diethyl tartrato(2-)]allylsilicate **5a***

A white solid (yield 56%); mp 55–58°C; $[\alpha]_D$=+14.07 (*c* 2.9, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3430 (NH), 2900, 1740 (C=O); $\delta_H$ ($CDCl_3$) 1.0–1.4 (m, 21H, $CH_3$), 1.6–1.7 (m, 2H, $CH_2Si$), 3.1–3.4 (m, 6H, $NCH_2$), 4.1–4.4 (m, 12H, $CH_2$, CH), 4.5–5.0 (m, 2H, $CH_2$=), 5.8–6.0 (m, 1H, CH=), 9.6 (bs, 1H, NH); $\delta_H$ ($CDCl_3$–$D_2O$) 1.02 (t, 9H, *J*=7.2 Hz, $NCH_2C\mathbf{H}_3$), 1.32 (t, 12H, *J*=7.0 Hz, $OCH_2C\mathbf{H}_3$), 1.62 (bs, 2H, $CH_2Si$), 2.53 (q, 6H, *J*=7.0 Hz, $NCH_2$), 4.30 (q, 8H, *J*=7.0 Hz, $OCH_2$), 4.54 (s, 4H, CH), 4.8–5.1 (m, 2H, $CH_2$=), 5.6–5.9 (bs, 1H, CH=); $\delta_C$ ($CDCl_3$) 8.1, 13.8, 24.9, 45.1, 60.2, 60.1, 71.9, 71.1, 109.6, 139.1, 173.2, 173.1; $\delta_{Si}$ −89.8. HR-MS *m*/*z* (FAB, negative ion) 477.1440 $(M-Et_3NH)^-$, calcd for $C_{19}H_{29}O_{12}Si$: 477.1434.

#### *4.1.2. Triethylammonium bis[(*R,R*)-diisopropyl tartrato(2-)]allylsilicate **5b***

A white solid (yield 55%); mp (tube-sealing) 45–47°C; $[\alpha]_D$=+9.85 (*c* 1.5, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3460 (NH), 3030 (C=**CH**), 1730 (C=O), 1620 (C=C); $\delta_H$ ($CDCl_3$) 1.1–1.4 (m, 33H, $CH_3$), 1.6–1.7 (m, 2H, $CH_2Si$), 3.0 (bs, 6H, $NCH_2$), 4.5 (s, 4H, CH), 4.6–5.2 (m, 6H, $CH_2$=, CH), 5.9–6.2 (m, 1H, C=CH-), 9.8 (bs, 1H, NH); $\delta_H$ ($CDCl_3$–$D_2O$) 1.02 (t, 9H, *J*=7.2 Hz, $NCH_2C\mathbf{H}_3$), 1.32 (d, 24H, *J*=6.1 Hz, $CHC\mathbf{H}_3$), 1.62 (bs, 2H, $CH_2Si$), 2.54 (q, 6H, *J*=7.2 Hz, $NCH_2$), 4.85 (s, 4H, CH), 5.18 (m, 4H, *J*=6.35 Hz, $C\mathbf{H}CH_3$), 4.82–5.85 (m, 3H, $C\mathbf{H}_2$=C**H**); $\delta_C$ ($CDCl_3$) 8.3, 21.6, 25.1, 45.3, 67.9, 67.8, 72.4, 71.3, 109.7, 139.6, 173.1, 172.9; $\delta_{Si}$ ($CDCl_3$) −89.2; HR-MS *m*/*z* (FAB, negative ion) 533.2042 $(M-Et_3NH)^-$, calcd for $C_{23}H_{37}O_{12}Si$: 533.2060.

### *4.2. General procedure for the reaction of **5** with aldehydes*

A mixture of chiral pentacoordinate allylsilicate **5b** (1.7 mmol) and aldehyde (1.5 mmol) in hexane (4 mL) was stirred at 60°C for 48 h. Then ethyl ether and hydrochloric acid (10%) were added to quench the reaction, followed by stirring for 1 h. The aqueous phase was extracted with ether (3×20 mL). The combined organic phases were washed with water (20 mL), aqueous KOH (1 M, 20 mL), water (3×20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography (ethyl acetate–petroleum ether) to afford the optically active homoallylic alcohol **4**.

### *4.3. General procedure of the allylation of aldehydes **9** with chiral diol-modified allyltrichlorosilane **8** or crotyltrichlorosilane **13** promoted by DMF*

To a flask charged with $CH_2Cl_2$ (60 mL) a solution of trichlorosilane **7** or crotyltrichlorosilane **13** (3 mmol) in $CH_2Cl_2$ (20 mL) and a solution of chiral diols **6** (3.3 mmol) in $CH_2Cl_2$ (20 mL) were added dropwise in a parallel addition mode at room temperature. The mixture was stirred for 12 h at room temperature and refluxed for 4 h, and then concentrated to ca. 3 mL, giving a solution of crude product **8** or **14**. DMF (3 mL) was added to the solution, followed by stirring for 1 h. The aldehyde **9** (2 mmol) was added, followed by stirring for 24 h at room temperature. Ether (40 mL) and saturated aqueous sodium bicarbonate (20 mL) were added to quench the reaction. The aqueous phase was extracted with ether (3×20 mL). The combined organic phases were washed with water (20 mL), aqueous potassium hydroxide (1 M, 20 mL), water (3×20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography (ethyl acetate–petroleum ether) to afford the homoallylic alcohol **4**.

#### *4.3.1. 1-Phenyl-3-buten-1-ol **4a***[15]

A colorless oil; $\nu_{max}/cm^{-1}$ 3380 (OH), 3060 (=C-H), 1635 (C=C); $\delta_H$ ($CDCl_3$) 2.10 (s, 1H, OH), 2.50 (t, 2H, *J*=7.0 Hz, $CH_2$), 4.71 (t, 1H, *J*=7.0 Hz, OCH), 5.10–5.20 (m, 2H, $CH_2$=), 5.64–5.86 (m, 1H, CH=), 7.20–7.40 (m, 5H, PhH); $\delta_C$ ($CDCl_3$) 43.8, 73.3, 118.3, 126.8, 127.5, 128.4, 134.4, 143.8.

#### *4.3.2. 1-Nonene-4-ol **4b***[16]

A colorless oil; $\nu_{max}/cm^{-1}$ 3350 (OH), 3060 (=CH-), 1630 (C=C); $\delta_H$ ($CDCl_3$) 0.89 (m, 3H, $CH_3$), 1.20–1.58 (m, 8H, $CH_2$), 1.87 (s, 1H, OH), 2.00–2.40 (m, 2H, $CH_2$), 3.64 (m, 1H, OCH), 5.05–5.20 (m, 2H, $CH_2$=), 5.73–5.98 (m, 1H, CH=); $\delta_C$ 14.0, 22.6, 25.3, 31.8, 36.7, 41.8, 70.6, 117.8, 134.8.

#### *4.3.3. 1-Dodecene-4-ol **4c***[17]

A colorless oil; $\nu_{max}/cm^{-1}$ 3350 (OH), 3060, 1635 (C=C); $\delta_H$ ($CDCl_3$) 0.88 (m, 3H, $CH_3$), 1.20–1.50 (m, 14H, $CH_2$), 2.12 (s, 1H, OH), 2.05–2.40 (m, 2H, $CH_2$), 3.62 (m, 1H, OCH), 5.00–5.20 (m, 2H, $CH_2$=), 5.70–5.90 (m, 1H, =CH); $\delta_C$ ($CDCl_3$) 14.0, 22.6, 25.6, 29.1, 29.5, 29.6, 31.8, 36.7, 41.8, 70.6, 117.7, 134.9.

### *4.4.* anti-*2-Methyl-1-phenyl-3-buten-1-ol* anti-***15***[8b]

A colorless oil, yield: 72%; $\nu_{max}/cm^{-1}$ 3402 (OH), 1635 (C=C), 1450; $\delta_H$ ($CDCl_3$) 0.89 (d, 3H, *J*=6.9 Hz), 2.40–2.59 (m, 1H), 4.35 (d, 1H, *J*=7.1 Hz), 5.17–5.23 (m, 2H), 5.75–5.87 (m, 1H), 7.27–7.37 (m, 5H).

### *4.5.* syn-*2-Methyl-1-phenyl-3-buten-1-ol* syn-***15***[8b]

A colorless oil, yield: 76%; $\nu_{max}/cm^{-1}$ 3400 (OH), 1635 (C=C), 1450; $\delta_H$ ($CDCl_3$) 1.02 (d, 3H, *J*=6.8 Hz), 2.54–2.65 (m, 1H), 4.60 (d, 1H, *J*=5.5 Hz), 5.04–5.08 (m, 2H), 5.71–5.83 (m, 1H), 7.26–7.38 (m, 5H).

The asymmetric allylation of glyoxylates **16** or **18** with trichlorosilanes **8** or **14** promoted by DMF were carried out under the conditions described above to give the corresponding α-homoallylic hydroxy ester.

### 4.6. (−)-Menthyl 2-hydroxy-4-pentenoate **17**

A colorless liquid; yield: 80%; $\nu_{max}/cm^{-1}$ 3450 (OH), 2900, 1720 (C=O), 1620, 1210; $\delta_H$ ($CDCl_3$) 0.71–0.78 (2d, 3H), 0.80–0.95 (m, 6H), 0.95–2.10 (m, 9H), 2.30–2.64 (m, 2H), 4.24 (dd, 1H, *J*=2.0, 6.4 Hz), 4.80 (dt, 1H, *J*=4.6, 6.4 Hz), 5.10–5.25 (m, 2H), 5.70–5.90 (m, 1H); $\delta_C$ ($CDCl_3$) (15.7, 16.2), (20.6, 20.8), 21.9, (22.8, 23.3), (25.8, 26.2), 31.3, 34.0, (38.6, 38.7), (40.6, 40.8), (46.8, 46.9), (69.6, 70.0), (75.9, 76.1), (118.6, 118.7), (132.3, 132.4), 174.0. The data in parentheses are from two diastereoisomers. Anal. calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.76; H, 10.28.

### 4.7. Butyl 2-hydroxy-4-pentenoate **19**

A colorless liquid; $[\alpha]_D$ −1.0 (*c* 4.4, $CHCl_3$); $\nu_{max}/cm^{-1}$ 3480 (OH), 3070, 1760 (C=O), 1635; $\delta_H$ ($CDCl_3$) 0.87 (3H, t, *J*=7.3 Hz), 1.20–1.50 (m, 2H), 1.55–1.70 (m, 2H), 2.18(s, 1H, OH), 2.35–2.80 (m, 2H), 4.12 (dt, 2H, *J*=2.0, 6.6 Hz), 4.19 (dd, 1H, *J*=4.8, 6.4 Hz), 5.05–5.22 (m, 2H), 5.7–5.9 (m, 1H); $\delta_C$ ($CDCl_3$) 13.6, 19.0, 30.6, 38.7, 65.5, 69.9, 118.7, 132.5, 174.5; *m*/*z* (EI) 172 ($M^+$, 1.9), 57 (100). Anal. calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.65; H, 9.27.

The procedure for ester-exchange reaction: To a solution of (−)-menthol (0.16 g, 1.0 mmol) in $CHCl_3$ (10 mL) *n*-butyl lithium (0.6 mL, 1.6 M in hexane, 1.0 mmol) was added at room temperature, followed by stirring for 30 min. A solution of **19** in $CHCl_3$ (5 mL) was added. The mixture was stirred for 12 h at room temperature and refluxed for 16 h, until the starting material **19** disappeared by TLC. The mixture was treated with saturated aqueous solution of sodium bicarbonate. The water phase was extracted by ether (3×30 mL). The combined organic phase was washed with brine (3×30 mL), dried over $MgSO_4$ and evaporated to give crude product. The crude product was purified with flash chromatography (silica gel, pet. ether:ethyl acetate as eluent) to give product **17**, 0.21 g, yield 85%.

### 4.8. syn-Butyl 2-hydroxy-3-methyl-4-pentenoate syn-**20**[23]

A colorless liquid, yield: 86%; $\nu_{max}/cm^{-1}$ 3498 (OH), 1730 (C=O), 1640; $\delta_H$ ($CDCl_3$) 0.87 (t, 3H, *J*=7.4 Hz), 0.94 (d, 3H, *J*=6.9 Hz), 1.32 (m, 2H), 1.57 (m, 2H), 2.61 (m, 1H), 2.64 (bs, 1H), 4.11 (m, 2H), 4.13 (d, 1H, *J*=3.2 Hz), 5.01–5.78 (m, 3H).

### 4.9. anti-Butyl 2-hydroxy-3-methyl-4-pentenoate anti-**20**[23]

A colorless liquid, yield: 87%; $\nu_{max}/cm^{-1}$ 3498 (OH), 1730 (C=O), 1640; $\delta_H$ ($CDCl_3$) 0.87 (t, 3H, *J*=7.4 Hz), 1.09 (d, 3H, *J*=6.9 Hz), 1.32 (m, 2H), 1.57 (m, 2H), 2.58 (m, 1H), 2.64 (bs, 1H), 4.04 (d, 1H, *J*=3.2 Hz), 4.11 (m, 2H), 5.01–5.78 (m, 3H).

### 4.10. General procedure for allylation of glyoxylates promoted by $TiCl_4$

To a solution of glyoxylate (2.5 mmol) in $CH_2Cl_2$ (15 mL) at −78°C was added dropwise the solution of $TiCl_4$ (2.5 mmol, 1.45 mL, 1.3 M in $CH_2Cl_2$). After stirring for 15 min, a solution of allylalkoxydimethylsilane **21**–**25** or crotyltrimethylsilane **31** in 3 mL of $CH_2Cl_2$ was added dropwise at the same temperature. The mixture was stirred at −78°C for 4 h, followed by hydrolysis with a saturated aqueous solution of $NH_4Cl$. The water phase was extracted by ether three times. The organic phase was washed with brine (3×10 mL), dried over $MgSO_4$ and filtered. The filtrate was evaporated and residue

was purified by flash chromatography using hexane–ethyl acetate as eluent to give the corresponding product, α-homoallylic hydroxy ester.

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