Asymmetric allylation of aldehydes with allyltrichlorosilane *via* a chiral pentacoordinate silicate

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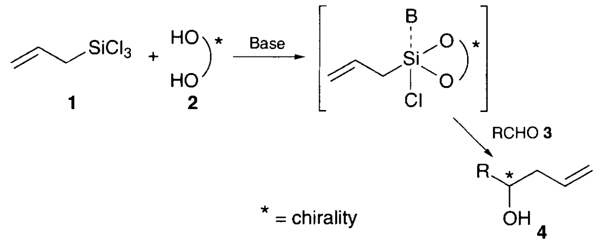
Asymmetric allylation of aldehydes with allyltrichlorosilane modified by a chiral diol *via* a chiral pentacoordinate silicate gave optically active alcohols with up to 71% ee.

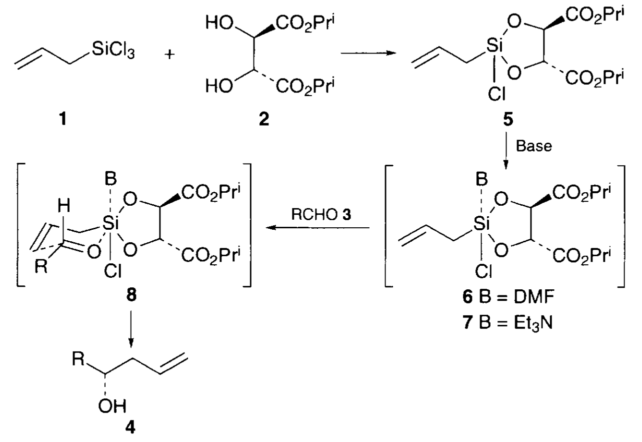
The allylation of carbonyl compounds with allylsilanes under Lewis acid conditions, first described by Sakurai and Hosomi,[1] has been extensively used in synthesis for the formation of C–C bonds.[2] The possibility of using this reaction for the asymmetric synthesis of optically active homoallylic alcohols has attracted considerable attention. However, for the reaction of aldehydes with both Si and C-centred chiral allylsilane, only modest enantioselectivity has been observed.[3] This was attributed to the reaction (under Lewis acid conditions) proceeding through a less rigid, open transition structure (an acyclic transition state). It was hoped that if the reaction could be made to proceed through a rigid six-membered cyclic transition state, higher asymmetric induction could be obtained. Sakurai[4] demonstrated that allylation of aldehydes with allyltrifluorosilane in the presence of hydroxy compounds and triethylamine, without a Lewis acid promoter, gave the corresponding homoallylic alcohols in a regio- and stereo-specific manner. Pentacoordinate allylsilicate intermediates with Lewis acid character and a cyclic transition state have been suggested as possible promoters.[5] However, the use of a chiral alcohol in the reaction of allyltrialkoxysilane with aldehydes through the same pathway gave poor selectivity (2–17% ee).[6] Kobayashi[7] reported that allyltrichlorosilane **1** could also react with aldehydes in DMF or some cosolvent mixtures *via* a pentacoordinate silicate intermediate and six-membered cyclic transition state. Recently, Denmark[8] employed chiral Lewis bases to promote asymmetric allylation, which improved the enantioselectivity markedly (up to 65% ee). We hoped that by using a chiral diol to modify allyltrichlorosilane in the Kobayashi reaction system, asymmetric allylation would proceed to give optically active homoallylic alcohols **4** with good enantioselectivity (Scheme 1).

(+)-(2*R*, 3*R*)-Diisopropyl tartrate **2** was treated with allyltrichlorosilane **1** in dichloromethane for 3 h at room temperature and 4 h at reflux, and then the mixture was concentrated to generate the crude product **5**. Without further purification, the reaction of **5** with aldehydes was carried out in Et_3N (3 equiv.)–CH_2Cl_2 or DMF–CH_2Cl_2 (1 : 1) at room temperature for 24 h, giving the corresponding optically active homoallylic alcohols **4** in reasonable overall yield (Table 1, Scheme 2).

Based on the known reaction of dichlorodimethylsilane with a tartrate species giving a cyclic silane,[9] the reaction of **1** with **2** should produce cyclic species **5**. A one-pot procedure for the reaction *via* the pentacoordinate silicate intermediate was recommended,[7,8] but residual achiral **1** in the crude product **5**



Scheme 1



Scheme 2

Table 1 Asymmetric allylation of aldehydes with **5**[a]

Entry	**3**, R	**1**:**2**:**3**	Solvent[b]	Yield of **4**[c] (%)	$[\alpha]_D$ of **4**/10^{-1} deg cm^2 g^{-1} (*c*, solv.)	Ee of **4** (%) (config.)[d]	Ref.
1	Ph	3:3:2	A	72	−12.6 (4.4, PhH)	27 (*S*)	12
2	pentyl	3:3:2	A	55	+3.6 (0.9, $CHCl_3$)	46[e] (*R*)	14
3	octyl	3:3:2	A	69	+4.7 (2.0, CCl_4)	44 (*R*)	15
4	Ph	3:3:2	B	50	−14.9 (2.4, PhH)	32 (*S*)	12
5	Ph	3:3.3:2	B	47	−18.0 (4.8, PhH)	39 (*S*)	12
6	octyl	3:3.3:2	B	47	+6.6 (4.5, CCl_4)	61 (*R*)	15
7	octyl	3:3.3:2	B	40	+7.6 (4.4, CCl_4)	71 (68[e]) (*R*)	15
8	pentyl	3:3.3:2	B	48	+4.3 (2.3, $CHCl_3$)	55 (*R*)	14

[a] Reaction conditions: room temp. for 24 h (−10 °C for 36 h for entry 7). [b] Cosolvent system: A, Et_3N (3 equiv.)–CH_2Cl_2; B, DMF–CH_2Cl_2 (1 : 1). [c] Isolated yield based on aldehydes. [d] Assigned by comparison with literature rotation values. [e] Determined by 400 MHz ^1H NMR analysis of the MTPA ester of **4** (ref. 13).

might reduce the enantioselectivity in the subsequent addition reaction with the aldehyde, so it is necessary to use chiral tartrate **2** in slight excess (*cf.* entry 4 *vs.* entry 5). The ^{29}Si NMR spectrum of **5** showed only one upfield peak at δ −170.3 in DMF and a downfield peak at δ 1.96 in $CDCl_3$, respectively. This provides evidence for the formation of a pentacoordinate silicate intermediate in the solution of **5** in DMF. On the other hand, there was no **1** present in the product **5** (^{29}Si NMR of **1**: δ 8.0 in $CDCl_3$).[7b] Apparently, a molecule of DMF, which plays the role of a Lewis base, participates in the coordination of the silicon atom of **5**, generating a chiral pentacoordinate silicate **6**. Similarly, a chiral pentacoordinate silicate **7** can be considered as an intermediate of the reaction, since Et_3N also has the ability to coordinate with the silicon atom.[10] The chiral pentacoordinate silicate **6** and **7** has enough Lewis acidity to undergo nucleophilic addition to aldehydes, giving the optically active homoallylic alcohols **4**, despite the DMF–CH_2Cl_2 and Et_3N–CH_2Cl_2 cosolvents. As shown in Table 1, the ee of the products **4** was up to 71%, reaching a level similar to that for asymmetric allylation using a chiral Lewis base as a promoter.[8] The enantioselectivity of the reaction promoted by DMF was better than that promoted by Et_3N. However, in the case of DMF, while the reaction proceeded smoothly, the yield was relatively low. Lower reaction temperature (−10 °C) could increase the ee slightly (entry 8), but the yield of **4** decreased. While the reaction of aromatic aldehydes proceeded in good yield, aliphatic aldehydes reacted sluggishly but with higher ee.

It is interesting to compare these results with the condensation reaction of C-centered chiral allylalkoxysilane with aldehydes promoted by a Lewis acid (~25% ee), which is suggested to proceed through an acyclic transition state.[11] The reaction of allyltrichlorosilane modified by a chiral tartrate, forming an analogue of the C-centered chiral allylalkoxysilane, with aldehydes in the presence of DMF or Et_3N gave higher enantioselectivity. The reason is that it proceeds through a chiral pentacoordinate transition state and subsequently a more rigid six-membered cyclic transition state **8** having chair conformation, as previously proposed.[5] The absolute configuration of the new chiral centre in the product **4** was deduced by comparison with literature rotation. The (*R*)-configurations of aliphatic **4** (R = alkyl) and (*S*)-configurations of the aromatic **4** (R = phenyl) are consistent with the stereochemical outcome of the proposed cyclic hexacoordinate silicon species. The direction of attack of the double bond in the allylsilane was to *Si* face of carbonyl group of the aldehyde. It is clear from the results of this investigation that the use of a chiral diol (to modify the allyltrichlorosilane), and DMF or Et_3N as the promoter, provides a convenient method for the synthesis of optically active homoallylic alcohols. Given that there is wide potential for the modification of the structure of the chiral diol, improvement of the enantioselectivity of the reaction can be predicted.

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