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Enantioselective Allylation of Aldehydes Catalyzed by Diastereoisomeric Bis(tetrahydroisoquinoline) *N*,*N*′-Dioxides

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Enantioselective allylation of aromatic and α,β-unsaturated aldehydes with allyltrichlorosilane catalyzed by two diastereoisomeric (*R*,R_{ax},*R*)- and (*R*,S_{ax},*R*)-bis-1,1′-[5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)isoquinoline] *N*,*N*′-dioxides was studied. The course of the reaction was profoundly influenced by the chosen solvent. The (*R*,S_{ax},*R*) catalyst efficiently promoted the reaction in THF with enantioselectivity up to 96 %. On the other hand, the allylation of aromatic aldehydes in the presence of the (*R*,R_{ax},*R*) catalyst proceeded only in MeCN (up to 67 % *ee*), and the level of asymmetric induction was strongly influenced by the presence of electron-donating and -accepting groups in the aldehyde. The allylation of α,β-unsaturated aldehydes proceeded only in dichloromethane (enantioselectivity up to 68 %).

Introduction

Enantioselective organocatalytic reactions have been in a spotlight of chemistry for more than a decade. This special attention is driven by several factors: (i) a catalyst can often be prepared easily from readily available enantiomerically pure starting material, (ii) catalysis is usually carried out under mild reaction conditions, (iii) catalysts do not contain metal atoms.[1] Although there are considerable potential benefits tied to the use of Lewis acid and/or base catalysts, the latter has been studied to a considerably lesser extent than the former.[2] Nonetheless, among Lewis base catalysts a special area is occupied by *N*-oxides. A considerable negative charge located on the oxygen atoms makes them highly basic molecules capable of interacting (activating) Lewis acids such as organosilanes.[3,4] Of numerous reactions, special attention is devoted to the enantioselective allylation of aldehydes, because it gives rise to chiral homoallyl alcohols that can serve as convenient building blocks for the synthesis of more complex compounds.[5] Typical examples include the syntheses of fluoxetine,[6] diospongine,[7] epicalyxin F,[8] rhoiptelol,[9] goniothalamin,[10] hyptolide,[11] fostriecine,[12] symbiodinolide,[13] and papulacandin D.[14] This resulted in the development of a series of organocatalysts having a chiral scaffold. These compounds could be roughly divided into three groups: (i) *N*,*N*′-dioxides with two pyridine moieties (most often bipyridines) possessing a stereogenic axis, (ii) *N*-oxides having the pyridine ring incorporated into various frameworks, and (iii) aliphatic *N*-oxides. The first group comprises 1,1′-bis(isoquinolyls) and 2,2′-bipyridyls.[15,16] In the second and structurally more diverse group, the pyridine ring can be fused with the terpene,[17,18] biaryl,[19] metallocene,[20] and paracyclophane frameworks,[21] or attached to a chiral binaphthyl unit through a linker.[22] The third group is represented by chiral pyrrolidine *N*-oxides.[23]

Recently, this laboratory developed a procedure for the synthesis of various axially chiral *N*,*N*′-dioxides with the bipyridine scaffold based on $CpCo(CO)_2$-catalyzed [2+2+2]-cyclotrimerization of alkynes (diynes) with nitriles under microwave irradiation. These included axially chiral pyridyl(tetrahydroisoquinoline)s,[22] isoquinolyl(tetrahydrosioquinoline)s,[25] symmetrically 3,3′-substituted bis(tetrahydroisoquinolyl)s,[26] and unsymmetrically 3,3′-substituted bis(tetrahydroisoquinolyl)s.[27,28] Unsymmetrically 3,3′-substituted bis(tetrahydroisoquinolyl)s, in particular, were proven to catalyze the highly enantioselective allylation of aromatic and α,β-unsaturated aldehydes with *ee* values reaching up to 99 %.

Furthermore, we showed that the appropriate choice of the reaction medium,[26,27a,28] that is, the solvent, was crucial for the course of the reaction and for asymmetric induction. In summary, although both reaction mechanisms proceed through six-membered transition states, electrophilic solvents (CH_2Cl_2, MeCN, etc.) promote the initial formation of pentacoordinate cationic silicon species, whereas nonelectrophilic solvents (toluene, THF, etc.) promote the formation of hexacoordinate neutral silicon species.[29] These observations and results thus provided the necessary background to understand the high level of asymmetric induction observed for allylations carried out in THF.[27a,28]

Taking into account the easy and fast preparation of (*R*,R_{ax},*R*)- and (*R*,S_{ax},*R*)-bis-1,1′-[5,6,7,8-tetrahydro-3-

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(tetrahydrofuran-2-yl)isoquinoline] *N*,*N*′-dioxides (**1**;[26] Figure 1) and the above-mentioned solvent effects, we decided to screen the enantioselective allylation of aromatic aldehydes in detail and also to check its scope in the case of α,β-unsaturated benzaldehydes.

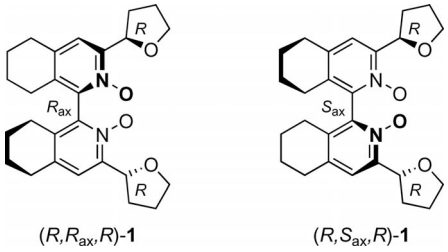
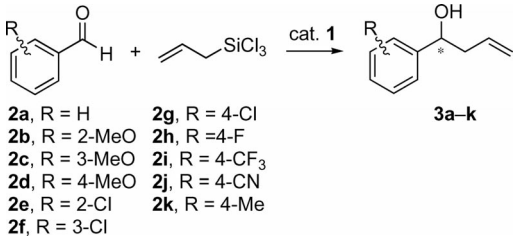


Figure 1. Diastereoisomeric bis(tetrahydroisoquinolyl) *N*,*N*′-dioxides (*R*,R_{ax},*R*)-**1** and (*R*,S_{ax},*R*)-**1**.

Results and Discussion

Initially, we decided to check the allylation of benzaldehydes **2** with allyltrichlorosilane under the previously used conditions with catalyst **1** (1 mol-%) at –78 °C (Scheme 1).



Scheme 1. Allylation of benzaldehydes **2** to homoallyl alcohols **3**.

Surprisingly, in the presence of (*R*,R_{ax},*R*)-**1** the reactions did not proceed at all. Then, allylation of selected aldehydes **2a** and **2d**–**i** with (*R*,S_{ax},*R*)-**1** was attempted. In this case, the allylation took place; however, yields of the corresponding homoallyl alcohols **3a** and **3d**–**i** after 24 h reaction time were rather marginal within the range of 2–6% (Table 1). On the other hand, the level of asymmetric induction was reasonable and was within the range 73–88% *ee* for **3a**, **3d**, and **3f**–**i**. The only exception was the allylation of 2-chlorobenzaldehyde (**2e**), where homoallyl alcohol **3e** was obtained in with only 40% *ee* (Table 1, Entry 5).

To increase the yields of the homoallyl alcohols, the amount of (*R*,S_{ax},*R*)-**1** was increased to 2 mol-% and the reaction temperature was raised to –40 °C. Over 11 variously substituted benzaldehydes bearing electron-donating or -accepting groups were subjected to the allylation with allyltrichlorosilane. In general, the reactions proceeded in good yields with high levels of asymmetric induction, regardless of the electronic properties of the substituents. It is also worth noting that an increase in the reaction temperature from –78 to –40 °C did not have any detrimental effect on the level of asymmetric induction. Thus, allylation of benzaldehyde (**2a**) and *para*-substituted benzaldehydes **2d** and **2g**–**k** yielded the corresponding products with *ee* values in the range 75–92% (Table 1, Entries 1, 4, 7–10). In a similar manner, the allylation of *meta*-substituted benzaldehydes **2c** and **2f** proceeded to give products **3c** and **3f** with 92 and 84% *ee*, respectively (Table 1, Entries 3 and 6). Only in the case of *ortho*-substituted benzaldehydes **2b** and **2e** was a lower level of asymmetric induction observed: 68% for **3b** and 25% for **3e** (Table 1, Entries 2 and 5).

The inability of (*R*,R_{ax},*R*)-**1** to catalyze the allylation of benzaldehydes in THF prompted us to switch the solvent to MeCN (Table 2). Gratifyingly, the altered reaction medium had a positive effect on the course of the reaction. The allylation of benzaldehydes **2a** and **2d**–**i** proceeded with full conversion, giving the corresponding homoallyl alcohols **3a** and **3d**–**i** quantitatively (Table 2, Entries 1–7). On the other hand, the level of asymmetric induction was highly dependent on the substituent attached to the aromatic ring. In the case of benzaldehyde (**2a**), the level of asymmetric induction was mediocre (48% *ee* for **3a**; Table 2, Entry 1). The presence of the electron-donating MeO substituent in the *para* position of **2d** resulted in an increased enantioselectivity of the allylation: 67% *ee* for **3d** (Table 2, Entry 2). However, the presence of electron-accepting groups led to a low or marginal level of asymmetric induction. Thus, allylation of **2f**–**h** furnished **3f**–**h** with *ee* values

Table 1. Allylation of aromatic aldehydes **2** to homoallyl alcohols **3** catalyzed by (*R*,S_{ax},*R*)-**1** in THF (24 h).

Entry	Aldehyde **2**	R	Product **3**	Reaction performed at –78 °C[a]		Reaction performed at –40 °C[b]	
				Yield [%][c]	*ee* [%][c]	Yield [%][c,d]	*ee* [%][c]
1	**2a**	H	**3a**	3	80 (*S*)	96	81 (*S*)
2	**2b**	2-MeO	**3b**			88	68 (*S*)
3	**2c**	3-MeO	**3c**			87	92 (*S*)
4	**2d**	4-MeO	**3d**	2	76 (*S*)	78	83 (*S*)
5	**2e**	2-Cl	**3e**	2	40 (*S*)	51	25 (*S*)
6	**2f**	3-Cl	**3f**	5	73 (*S*)	80	84 (*S*)
7	**2g**	4-Cl	**3g**	6	87 (*S*)	87	89 (*S*)
8	**2h**	4-F	**3h**	5	88 (*S*)	90	92 (*S*)
9	**2i**	4-CF_3	**3i**	5	80 (*S*)	75	75 (*S*)
10	**2j**	4-CN	**3j**			86	92 (*S*)
11	**2k**	4-Me	**3k**			86	88 (*S*)

[a] Reactions were catalyzed by 1 mol-% of (*R*,S_{ax},*R*)-**1**. [b] Reactions were catalyzed by 2 mol-% of (*R*,S_{ax},*R*)-**1**. [c] Determined by GC. [d] Isolated yields were on average lower by 10–15%.

Table 2. Allylation of benzaldehydes **2** to homoallyl alcohols **3** catalyzed by (R,R_{ax},R)-**1** and (R,S_{ax},R)-**1** in MeCN (–40 °C, 24 h).

Entry	Aldehyde **2**	R	Product **3**	(R,R_{ax},R)-**1**[a]		(R,S_{ax},R)-**1**[a,b]	
				Yield [%][c,d]	*ee* [%][c]	Yield [%][c,d]	*ee* [%][c]
1	**2a**	H	**3a**	>98	48 (*S*)	>98	46 (*R*)
2	**2d**	4-MeO	**3d**	>98	67 (*S*)	>98	0
3	**2e**	2-Cl	**3e**	>98	2 (*S*)		
4	**2f**	3-Cl	**3f**	>98	26 (*S*)		
5	**2g**	4-Cl	**3g**	>98	32 (*S*)		
6	**2h**	4-F	**3h**	>98	50 (*S*)		
7	**2i**	4-CF_3	**3i**	>98	9 (*S*)	>98	16 (*R*)

[a] Reactions were catalyzed by 1 mol-% of **1**. [b] The data were taken from ref.[26a] [c] Determined by GC. [d] Isolated yields were on average lower by 10–15%.

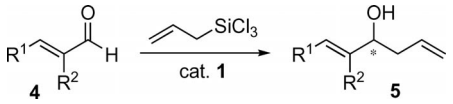
in the range 26–50% (Table 2, Entries 4–6) and that of **2e** and **2i** yielded **3e** and **3i** with 2 and 9%*ee*, respectively (Table 2, Entries 3 and 7). The previously reported allylations catalyzed with (R,S_{ax},R)-**1** in MeCN are added for comparison.[26a] Although the yields of homoallyl alcohols were quantitative, the level of asymmetric induction was low: **3a** was obtained with 46%*ee* (Table 2, Entry 1) and **3i** in 16%*ee* (Table 2, Entry 7). Surprisingly, the allylation of **2b** did not result in any asymmetric induction at all (Table 2, Entry 2).

Comparison of the allylations of aromatic aldehydes carried out in THF and MeCN clearly supports previous observations and the conclusion that the solvent crucially affects the course of the reaction as well as the level of asymmetric induction. The reactions carried out with catalysts possessing an (*R*) stereogenic axis gave rise to products with (*R*) configuration, whereas those carried out with an (*S*) stereogenic axis proceeded to give products with (*S*) configuration. In MeCN, the opposite was true: the catalyst with an (*R*) stereogenic axis yielded products with (*S*) configuration and vice versa. For the reactions carried out in THF, the electronic properties of the substituents attached to the aromatic ring did not have any substantial effect on the level of asymmetric induction, whereas in MeCN, benzaldehydes bearing electron-donating substituents (MeO) were allylated with a higher level of enantioselectivity than those bearing electron-accepting groups (Cl, F). This trend has already been observed by others.[15a,16b]

We recently showed that allylation of α,β-unsaturated aldehydes catalyzed by unsymmetrically 3,3′-substituted bis(tetrahydroisoquinolyl)s could proceed with enantioselectivity up to 99%*ee*.[28] In this respect, the comparison of catalytic activity and the level of asymmetric induction achieved in the presence of **1** was interesting (Table 3).

At the outset, allylation of cinnamaldehydes **4a**–**g** catalyzed by (R,S_{ax},R)-**1** in THF was carried out at –40 °C. As expected, the absolute configuration of the corresponding homoallyl alcohols **5** was *S*. Rather mediocre enantioselectivity was observed in the allylations of cinnamaldehyde (**4a**, 66%*ee*) and 4-methoxycinnamaldehyde (**4b**, 63%*ee*), which bear electron-donating group (Table 3, Entries 1 and 2). The presence of electron-accepting groups in **4c**–**e** led to an increase in asymmetric induction: 94%*ee* for **5c**, 79%*ee* for **5d**, and 72% *ee* for **5e** (Table 3, Entries 3–5). Gratifyingly, the presence of substituents in the α-position (chloro and methyl groups) to the carbonyl group in **4f** and **4g** led to products **5f** and **5g** with high enantioselectivity (96%*ee*; Table 3, Entries 6 and 7), which was higher than those obtained previously.[26] The allylation of aliphatic α,β-unsaturated aldehydes **4h** and **4i** bearing a methyl group at the α-position led to products **5h** and **5i** with *ee* values of 70 and 80%*ee*, respectively.

Table 3. Allylation of α,β-unsaturated aldehydes with (R,R_{ax},R)-**1** and (R,S_{ax},R)-**1** in THF and dichloromethane (–40 °C, 3–6 h).



Entry	Aldehyde **4**	R^1	R^2	Product **5**	(R,S_{ax},R)-**1**[a] in THF		(R,R_{ax},R)-**1**[a] in CH_2Cl_2	
					Yield [%][b]	*ee* [%][c]	Yield [%][b]	*ee* [%][c]
1	**4a**	C_6H_5	H	**5a**	70	66 (*S*)	55	23 (*S*)
2	**4b**	4-$MeOC_6H_4$	H	**5b**	53	63 (*S*)	40	28 (*S*)
3	**4c**	4-BrC_6H_4	H	**5c**	75	94 (*S*)	97	15 (*S*)
4	**4d**	4-FC_6H_4	H	**5d**	58	79 (*S*)	82	17 (*S*)
5	**4e**	4-$NO_2C_6H_4$	H	**5e**	73	72 (*S*)[d]	93	4 (*S*)[d]
6	**4f**	C_6H_5	Me	**5f**	82	96 (*S*)	95	68 (*S*)
7	**4g**	C_6H_5	Cl	**5g**	60	96 (*S*)	60	62 (*S*)
8	**4h**	Me	Me	**5h**	52	70 (*R*)	50	61 (*R*)
9	**4i**	Et	Me	**5i**	60	80 (*R*)	50	62 (*R*)

[a] Reactions were catalyzed by 1 mol-% of **1**. [b] Determined by NMR spectroscopy (isolated yields were on average lower by 10–15%). [c] Determined by GC. [d] Determined by HPLC.

The (R,R_{ax},R)-**1**-catalyzed allylation reaction of cinnamaldehydes **4** in THF did not proceed as it did for the benzaldehyde substrates. Interestingly, the reaction also did not take place in MeCN. Fortunately, switching the reaction medium to CH_2Cl_2 resulted in a smooth reaction. On the other hand, an increase in the catalytic activity had a detrimental effect on the level of enantioselectivity. Thus, the observed level of asymmetric induction for the allylation of cinnamaldehydes **4a**–**d** was rather low (15–28%*ee*; Table 3, Entries 1–4). In the case of 4-nitrocinnamaldehyde, the asymmetric induction was marginal (4%*ee*; Table 3, Entry 5). Only in the case of cinnamaldehydes **4f** and **4g** did the enantioselectivity reach 68 and 62%*ee*, respectively (Table 3, Entries 6 and 7). A similar enantioselectivity was observed also in the allylation of α,β-unsaturated aldehydes **4h** and **4i**, which gave rise to homoallylic alcohols **5h** (61%*ee*) and **5i** (62%*ee*).

The dramatic difference in the level of asymmetric induction in the allylations in THF and in MeCN or dichloromethane can be reasonably explained by different reaction mechanisms. In the former solvent, the existence of a neutral hexacoordinate silicon intermediate is presumed to be responsible for a more conformationally rigid transition state, whereas in the case of the latter solvent, the course of the reaction proceeds through a cationic pentacoordinate species that gives rise to conformationally more flexible intermediates.[29]

On the other hand, despite the current level of knowledge regarding the role of the structure of the catalyst used, as well as that of a solvent, on the course of the reaction and the level of asymmetric induction on experimental as well as theoretical levels,[19b,28,29] practical experiments still confirm that there is a number of subtle effects that may crucially control the overall outcome. A typical example is the lack of catalytic activity of (R,R_{ax},R)-**1** in the allylation of benzaldehydes in THF and that of cinnamaldehydes in THF and MeCN. Although there is no evidence, participation of the oxygen atom belonging to the chiral tetrahydrofuran moiety in the coordination to allyltrichlorosilane to form a coordinatively saturated silicon species that is not able to react with the aldehyde cannot be excluded. On the other hand, a pleasant surprise was the high level of asymmetric induction observed in the case of the allylation of α-substituted cinnamaldehydes **4f** and **4g**, which could be explained by the existence of a more conformationally rigid transition state resulting in more selective chirality transfer.

Conclusions

The results presented clearly emphasize several points. Firstly, 3,3′-substituted bis(tetrahydroisoquinolyl)s could be used for the highly enantioselective allylation of benzaldehydes bearing electron-donating or -accepting groups with up to 92%*ee* (Table 1, Entries 3, 8, and 10). They could also be used for the highly enantioselective allylation of *para*-substituted cinnamaldehydes bearing electron-withdrawing groups (Table 3, Entry 3) and α-substituted cinnamaldehydes with up to 96%*ee* (higher asymmetric induction in comparison with other related catalysts;[28] Table 1, Entries 6 and 7). Secondly, solvent effects play an important role, which, in spite of the current knowledge, is still difficult to fully comprehend. Thirdly, a fast and easy synthetic route to catalysts **1** on the preparative scale from commercially available compounds could make them useful synthetic tools in asymmetric synthesis.

Experimental Section

General Procedure for the Enantioselective Allylation of Benzaldehydes 2 with Allyltrichlorosilane Catalyzed by 1: To a solution of **1** (0.005 or 0.0025 mmol), a benzaldehyde (0.25 mmol), diisopropylethylamine (54 μL, 0.31 mmol) in a solvent (0.5 mL) at –40 °C (or –78 °C) was added allyltrichlorosilane (46 μL, 0.31 mmol), and the reaction mixture was stirred for 24 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (1 mL), and the organic layer was separated and dried with $MgSO_4$. Yields and *ee* values were determined by GC (HP-Chiral β, 30 m × 0.25 mm, oven: 80 °C for 1 min, then 1 °C/min to 160 °C, 5 min at that temperature, flow: 1.5 mL/min). Spectral characteristics of the prepared compounds were in agreement with the previously reported data.[24a,25]

General Procedure for the Enantioselective Allylation of Benzaldehydes 2 with Allyltrichlorosilane Catalyzed by 1: To a solution of **1** (0.004 mmol), an α,β-unsaturated aldehyde (0.4 mmol), diisopropylethylamine (104 μL, 0.6 mmol) in a solvent (2 mL) at –40 °C was added allyltrichlorosilane (85 μL, 0.6 mmol), and the reaction mixture was stirred for 3–6 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (1 mL), and the organic layer was separated and dried with $MgSO_4$. Yields and *ee* values were determined by GC (HP-Chiral β, 30 m × 0.25 mm, oven: 80 °C for 1 min, then 1 °C/min to 160 °C, 5 min at that temperature, flow: 1.5 mL/min). Spectral characteristics of the prepared compounds were in agreement with the previously reported data.[24a,25]

Supporting Information (see footnote on the first page of this article): Experimental details.

Acknowledgments

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