Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters 46 (2005) 157–159
Tetrahedron Letters

Chiral phosphine oxide BINAPO as a catalyst for enantioselective allylation of aldehydes with allyltrichlorosilanes

Makoto Nakajima,[a,*] Shunsuke Kotani,[a,b] Tadao Ishizuka[a] and Shunichi Hashimoto[b]

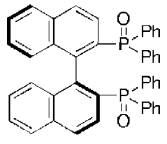
[a]*Faculty of Medical and Pharmaceutical Sciences, Kumamoto University, Kumamoto 862-0973, Japan*
[b]*Graduate School of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan*

Received 6 October 2004; revised 25 October 2004; accepted 27 October 2004

Abstract—The effectiveness of chiral phosphine oxide BINAPO as a catalyst for the enantioselective addition of allyltrichlorosilanes to aldehydes was demonstrated, wherein the combination of diisopropylethylamine and tetrabutylammonium iodide as additives is crucial for accelerating the catalytic cycle.

The asymmetric allylation of carbonyl compounds to generate two successive stereogenic centers has been the subject of investigation in recent years.[1] While high enantioselectivities have been achieved with allylmetals in the presence of chiral Lewis acids as catalysts,[2] these processes preferentially afford *syn* homoallylic alcohols from both stereoisomers of allylmetals via acyclic transition states. On the other hand, Lewis base-catalyzed allylations with allyltrichlorosilanes are presumed to proceed via chair-like transition states that involve hypervalent silicates,[3,4] in which the addition of (*E*)- and (*Z*)-silane provide the *anti*- and *syn*-product, respectively, with high diastereoselectivity. Asymmetric versions of the Lewis base-catalyzed allylations using chiral phosphoramide,[5] formamide,[6] and pyridine *N*-oxide[7] derivatives as catalysts were reported to afford the homoallylic alcohols with good enantioselectivities.[8] Although phosphine oxides possess a notable electron-pair donor property and form complexes with various metals,[9] less attention has been paid to chiral phosphine oxides in the field of asymmetric catalysis.[10] Quite recently, Kobayashi and co-workers reported an allylation of acylhydrazones with allyltrichlorosilane promoted by achiral phosphine oxides, that required stoichiometric amounts of phosphine oxides as promoters.[11] Herein we describe the first enantioselective allylation of aldehydes with allyltrichlorosilanes promoted by substoichiometric amounts of chiral phosphine oxide.

We initially investigated the allylation of benzaldehyde with allyltrichlorosilane at rt in dichloromethane using 10 mol% of BINAPO,[10c] a precursor of BINAP which is the most common chiral phosphine ligand. The reaction did proceed, however, the catalytic activity was so low that only 32% of homoallyl alcohol was obtained after 24 h. (Table 1, entry 1). We previously reported that the addition of diisopropylethylamine significantly enhanced *N*-oxide-promoted allylation with allyltrichlorosilane.[7a] In fact the addition of the amine increased the reactivity of BINAPO, but the yield of the alcohol was still modest (entry 2). After considerable screening, we found the addition of tetrabutylammonium iodide[12] to the above system dramatically increased the reactivity (entry 4).[13] Since the addition of tetrabutylammonium iodide alone does not give comparable result (entry 3), the combination of diisopropylethylamine and tetrabutylammonium iodide was proved to be essential for the reactivity, although the details are unclear.



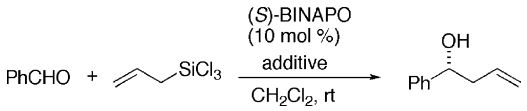
(*S*)-BINAPO

With appropriate additives in hand, we then examined allylations of benzaldehyde with trichlorosilanes of various substituent patterns. As shown in Table 2, γ-allylated *syn*-homoallylic alcohol was obtained from (*Z*)-crotyltrichlorosilane (entry 1) while the corresponding *anti*-alcohol was produced from (*E*)-crotyltrichlorosilane (entry 2). These results suggest that these allylations

Keywords: Allylation; Catalyst; Enantioselectivity; Phosphine oxide.
* Corresponding author. Tel.: +81 96 371 4680; fax: +81 96 362 7692; e-mail: nakajima@gpo.kumamoto-u.ac.jp

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.10.168

Table 1. Effect of additives in BINAPO-catalyzed allylation



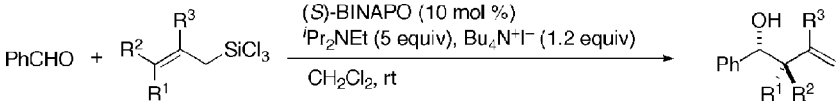
Entry	Additive (equiv)	Time (h)	Yield (%)[a]	Ee (%)[b]
1	None	24	32	36
2	$^{i}Pr_2NEt(5)$	24	79	37
3	$Bu_4N^+I^-(1.2)$	12	54	46
4	$^{i}Pr_2NEt(5) + Bu_4N^+I^-(1.2)$	4	92	43

[a] Isolated yield.
[b] Determined by HPLC (Daicel Chiralcel OD).

mediated by BINAPO proceed via cyclic chair-like transition structures that involve hypervalent silicates. The enantioselectivity strongly depended on substituent pattern on allylsilane. *trans*-Crotylsilane gave a selectivity similar to that of the parent allylsilane (entry 2), while *cis*-crotylsilane (entry 1) and prenylsilane (entry 3) dramatically decreased the enantioselectivity. It is noteworthy that the reaction of β-substituted silanes (entries 4–6), which gave lower selectivities with other Lewis bases,[7a] afforded the adducts in good enantioselectivities.

Table 3 summarizes the results obtained in the reaction of a variety of aldehydes with methallyltrichlorosilane. Allylation of aromatic aldehydes gave results similar to those with benzaldehyde (entries 1–7). Although the electronic factor on benzene ring does not significantly affect the enantioselectivity (entries 1, 2, 6, and 7), α,β-unsaturated aldehydes, and aliphatic aldehydes were unsuitable substrates in terms of both chemical yield and enantioselectivity (entries 10, 11). The best enantio-

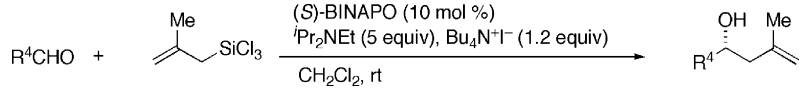
Table 2. BINAPO-catalyzed allylation with trichlorosilanes



Entry	R^1	R^2	R^3	Time (h)	Yield (%)[a]	Ee (%)[b](confgn)[c]	$[\alpha]_D$ (*c*, solvent)
1[d]	Me	H	H	4	92[e]	4 (1*S*,2*R*)	−2.3 (0.56, $CHCl_3$)
2[f]	H	Me	H	2	87[g]	46 (1*R*,2*R*)	+44.7 (0.75, $CHCl_3$)
3	Me	Me	H	4	63	4 (*R*)	+2.3 (0.95, $CHCl_3$)
4	H	H	Me	1	73	66 (*R*)	+40.0 (0.58, C_6H_6)
5	H	H	Ph	1	80	59 (*R*)	−16.7 (1.72, $CHCl_3$)
6	H	$-(CH_2)_4-$		3	81	64	+40.2 (1.17, $CHCl_3$)

[a] Isolated yield.
[b] Determined by HPLC (Daicel Chiralcel OD-H or Chiralpak AD-H).
[c] Configuration assignment by comparison to the literature values of optical rotations, see Supplementary Data.
[d] *E*:*Z* = 1:99.
[e] *syn*:*anti* = 99:1.
[f] *E*:*Z* = 77:23.
[g] *syn*:*anti* = 23:77.

Table 3. BINAPO-catalyzed methallylation of aldehydes



Entry	R^4	Time (h)	Yield (%)[a]	Ee (%)[b] (confgn)[c]	$[\alpha]_D$ (*c*, solvent)
1	4-ClC_6H_4	2	77	65 (*R*)	+34.7 (0.55, Et_2O)
2	4-$MeOC_6H_4$	1	75	55 (*R*)	+42.4 (0.45, C_6H_6)
3	2-Furyl	1	53	63 (*R*)	+31.7 (0.49, $CHCl_3$)
4	1-Naphthyl	4	57	53	+59.8 (0.54, $CHCl_3$)
5	2-Naphthyl	4	75	62	+56.7 (0.51, $CHCl_3$)
6	3,5-$(CF_3)_2C_6H_3$	4	65	56	+26.4 (0.89, $CHCl_3$)
7	3,4,5-$(MeO)_3C_6H_2$	4	61	57	+27.0 (1.15, $CHCl_3$)
8	3,5-$Me_2C_6H_3$	2	67	71	+43.8 (0.97, $CHCl_3$)
9[d]	3,5-$Me_2C_6H_3$	72	70	79	+46.2 (1.19, $CHCl_3$)
10	PhCH=CH	1	67	32 (*R*)	+13.5 (0.39, C_6H_6)
11	$PhCH_2CH_2$	24	59	29 (*S*)	−5.7 (1.0, $CHCl_3$)

[a] Isolated yield.
[b] Determine by HPLC (Daicel Chiralcel OD-H, OJ-H or Chiralpak AD-H).
[c] Configuration assignment by comparison to literature values of optical rotations, see Supplementary data.
[d] The reaction was conducted at −23 °C.

selectivity (79% ee) was observed in the reaction of 3,5-dimethylbenzaldehyde at −23 °C (entry 9).

In summary, we have demonstrated the effectiveness of chiral phosphine oxide BINAPO as a catalyst for the enantioselective addition of allyltrichlorosilanes to aldehydes, wherein a combination of diisopropylethylamine and tetrabutylammonium iodide as additives is crucial for accelerating the catalytic cycle. The present reaction provides the first example that utilizes chiral phosphine oxide as a catalyst in the enantioselective reaction. Studies on the mechanism as well as the design of chiral phosphine oxides to further enhance enantioselectivity are currently in progress.

Acknowledgments

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan and SUNBOR GRANT.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.10.168.

References and notes

1. For reviews on asymmetric allylation of carbonyl compounds, see: (a) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 489–594; (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207–2293; (c) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31–47.
2. For a review on chiral Lewis acid-catalyzed allylation of aldehydes, see: Cozzi, P. G.; Tagliavini, E.; Umani-Ronchi, A. *Gazz. Chim. Ital.* **1997**, *127*, 247–254.
3. (a) Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453–3456; (b) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620–6628.
4. For recent reviews on hypervalent silicates, see: (a) Sakurai, H. *Synlett* **1989**, 1–8; (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448.
5. (a) Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161–6162; (b) Iseki, K.; Kuroki, Y.; Takahashi, M.; Kobayashi, Y. *Tetrahedron Lett.* **1996**, *37*, 5149–5150.
6. Iseki, K.; Mizuno, S.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron Lett.* **1998**, *39*, 2767–2770.
7. (a) Nakajima, M.; Saito, M.; Shiro, M.; Hashimoto, S. *J. Am. Chem. Soc.* **1998**, *120*, 6418–6419; (b) Malkov, A. V.; Orsini, M.; Pernazza, D.; Muir, K. W.; Langer, V.; Meghani, P.; Kocovsky, P. *Org. Lett.* **2002**, *4*, 1047–1050; (c) Shimada, T.; Kina, A.; Ikeda, S.; Hayashi, T. *Org. Lett.* **2002**, *4*, 2799–2803.
8. For a review on asymmetric allylations catalyzed by chiral Lewis bases, see: Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763–2793.
9. Grushin, V. V. *Chem. Rev.* **2004**, *104*, 1629–1662.
10. Mono(phosphine oxide)–Pd complex: (a) Dai, W.-M.; Yeung, K. K. Y.; Leung, W. H.; Haynes, R. K. *Tetrahedron: Asymmetry* **2003**, *14*, 2821–2826, Bis(phosphine oxide)–Fe complex; (b) Matsukawa, S.; Sugama, H.; Imamoto, T. *Tetrahedron Lett.* **2000**, *41*, 6461–6465, Bis(phosphine oxide)–Sm complex; (c) Mikami, K.; Yamaoka, M. *Tetrahedron Lett.* **1998**, *39*, 4501–4504, For Hybrid phosphine oxide ligand, see Ref. 9.
11. Ogawa, C.; Konishi, H.; Sugiura, M.; Kobayashi, S. *Org. Biomol. Chem.* **2004**, *2*, 446–448.
12. Short, J. D.; Attenoux, S.; Berrisford, D. J. *Tetrahedron Lett.* **1997**, *38*, 2351–2354.
13. Typical procedure: A solution of benzaldehyde (50 mg, 0.47 mmol) in CH_2Cl_2 (0.5 mL), diisopropylethylamine (0.41 mL, 2.4 mmol), and allyltrichlorosilane (0.10 mL, 0.69 mmol) were successively added to a solution of (*S*)-BINAPO (32 mg, 0.028 mmol) and tetrabutylammonium iodide (207 mg, 0.56 mmol) in CH_2Cl_2 (0.5 mL) at room temperature (20–25 °C). After stirring for 4 h, the reaction was quenched by 10% NaOH (1 mL). The mixture was extracted with AcOEt (30 mL) and the organic layer was successively washed with 10% HCl (10 mL), satd $NaHCO_3$ (10 mL), and brine. Drying over Na_2SO_4 and evaporating the solvent furnished the crude product, which was purified by column chromatography (SiO_2 7 g, hexane/AcOEt = 12/1) to give the alcohol (63.5 mg, 92%, $[\alpha]_D$ +21.8 (*c* 0.96, C_6H_6)) as a colorless oil. Ee was determined to be 43% by chiral HPLC (Daicel Chiralcel OD, 1 mL/min, hexane/2-propanol = 40:1).