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Asymmetric Allylation of Aldehydes Catalyzed by Substoichiometric Amounts of Chiral Phosphoramides

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Abstract: *The asymmetric allylation and crotylation of aromatic aldehydes with allylic trichlorosilanes catalyzed by substoichiometric quantities of chiral phosphoramides were carried out with good enantiomeric excess (up to 88% ee). Phosphoramides 3 and 4, prepared from (S)-proline, gave chiral homoallylic alcohols 6 and their enantiomers 7, respectively, with similar levels of enantioselectivity.*

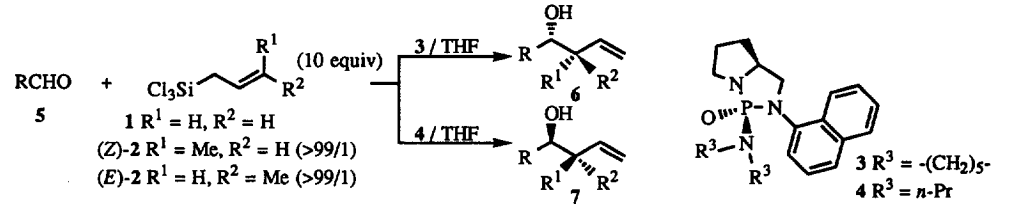
The asymmetric addition of allylmetal reagents to aldehydes has proven to be a very effective means for synthesizing chiral homoallylic alcohols.[1] Several asymmetric allylations with allylsilanes[2] and -stannanes[3] catalyzed by chiral Lewis acids have been reported and these transformations provide chiral *syn* homoallylic alcohols with high diastereoselectivity from either stereoisomer of crotylsilanes and -stannanes. Denmark *et al.* noted the asymmetric allylation of aromatic aldehydes with allylic trichlorosilanes (**1** and **2**) to be promoted by chiral phosphoramides as Lewis bases in high yield but modest enantiomeric excess[4] and this method gives *syn* and *anti* homoallylic alcohols diastereoselectively from (*Z*)- and (*E*)-crotyltrichlorosilane, respectively. This paper presents preliminary examples of the use of substoichiometric quantities of chiral phosphoramides **3** and **4**, prepared from (*S*)-(-)-proline, which promote the allylation and crotylation of aromatic aldehydes with high diastereoselectivity and good enantiomeric excess (up to 88% ee).

Chiral phosphoramides **3** and **4** were prepared from (*S*)-2-[(α-naphthylamino)methyl]pyrrolidine[5] with the corresponding phosphoramidic dichlorides as described by Peyronel *et al.*[6] and their absolute configurations were determined by X-ray crystallography. In a typical reaction, allylic trichlorosilane (**1** or **2**, 10 mmol) was added dropwise to a solution of aldehyde **5** (1 mmol) and phosphoramide (**3** or **4**, 0.1-0.2 mmol) in tetrahydrofuran (2 ml) at -60 or -78°C. The reaction mixture was stirred at -60 or -78°C for 72-168 h and added to saturated aqueous sodium hydrogen carbonate to quench the reaction. The corresponding product, homoallylic alcohol **6** or **7**, was purified by flash chromatography (*n*-hexane-ethyl acetate) and enantiomeric excess was determined by HPLC using a chiral column or ^{1}H NMR of the corresponding (*R*)-MTPA ester. The results are summarized in Table 1. The absolute configurations of homoallylic alcohols, **6a**, **6d**, **6e**, **7a**, **7d** and **7e** were established by comparison with literature values.[7,8] Phosphoramide **3** promoted the allylation of aldehydes **5a** and **5b** with allyltrichlorosilane **1** in good enantiomeric excess, while aldehyde **5c** was less effective with respect to yield and enantioselectivity (entries 1-3). Crotylation of aldehydes **5a** and **5d** with (*Z*)- and (*E*)-2-propenyltrichlorosilane, (*Z*)-**2** and (*E*)-**2**, using **3** proceeded at -60°C to afford the corresponding homoallylic alcohols (**6d-f**) with high diastereoselectivity and good enantiomeric excess (entries 4-6). In the same manner, the allylation and crotylation catalyzed by phosphoramide **4** were carried out with good enantioselectivity (entries 7-12) and the allylation of benzaldehyde (**5a**) gave the highest enantiomeric excess (88% ee, entry 7). Of greater interest is that phosphoramide **4** provided the enantiomers of the homoallylic alcohols given by phosphoramide **3** with similar enantioselectivity (**6a**, **6b** and **6d-f** vs. **7a**, **7b** and **7d-f**).

In conclusion, this paper presents potential applications of chiral Lewis bases easily prepared from (*S*)-proline in asymmetric allylation. The yields and enantioselectivities with substoichiometric amounts of

phosphoramides **3** and **4** are satisfactory. Further study to improve optical yield and elucidate reaction mechanisms is now in progress.

Table 1. Allylation and Crotylation Using Substoichiometric Amounts of Chiral Phosphoramides **3**, and **4**



Entry	Aldehyde		Silane	Catalyst	Temp.	Time	Product		
	5	R		(mol%)	(°C)	(h)		yield[a] % (syn/anti)[b]	ee % (config)[c]
1	**a**	C_6H_5	**1**	**3** (10)	-78	168	**6a**	67	85[d] (*R*)[7]
2	**b**	2-MeC_6H_4	**1**	**3** (20)	-60	72	**6b**	89	80[d]
3	**c**	4-$CF_3C_6H_4$	**1**	**3** (20)	-60	72	**6c**	47	72[e]
4	**a**	C_6H_5	(*Z*)-**2**	**3** (20)	-60	96	**6d**	95 (98/2)	76[e] (1*R*,2*S*)[8]
5	**a**	C_6H_5	(*E*)-**2**	**3** (20)	-60	96	**6e**	68 (3/97)	73[e] (1*R*,2*R*)[8]
6	**d**	4-*t*-BuC_6H_4	(*Z*)-**2**	**3** (20)	-60	120	**6f**	52 (>99/1)	82[e]
7	**a**	C_6H_5	**1**	**4** (10)	-78	168	**7a**	83	88[d] (*S*)[7]
8	**b**	2-MeC_6H_4	**1**	**4** (20)	-60	72	**7b**	86	81[d]
9	**a**	C_6H_5	(*Z*)-**2**	**4** (20)	-60	96	**7d**	80 (98/2)	77[e] (1*S*,2*R*)[8]
10	**a**	C_6H_5	(*E*)-**2**	**4** (20)	-60	96	**7e**	90 (2/98)	83[e] (1*S*,2*S*)[8]
11	**b**	2-MeC_6H_4	(*Z*)-**2**	**4** (20)	-60	120	**7g**	78 (>99/1)	83[e]
12	**d**	4-*t*-BuC_6H_4	(*Z*)-**2**	**4** (20)	-60	120	**7f**	72 (95/5)	82[e]

a) Isolated yields based on the starting aldehydes; b) Determined by ^1H NMR; c) Absolute configuration of the major enantiomer was established by comparison with the literature; d) Determined by HPLC using a Daicel Chiralcel OD-H or AD column; e) Determined by ^1H NMR of the corresponding (*R*)-MTPA ester.

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