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Enantioselective Addition of Chirally Modified Allylboranes to *N*-(Trimethylsilyl)benzaldehyde Imine

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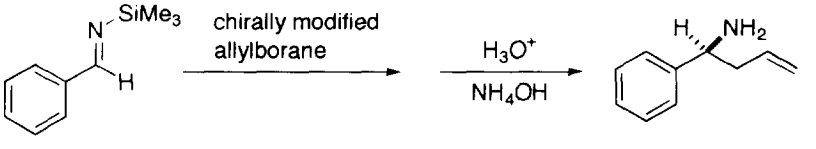
Abstract: *Enantioselective allylation of N-(trimethylsilyl)benzaldehyde imine has been investigated by the use of optically active allylboron reagents including dialkyl 2-allyl-1,3,2-dioxaborolane-4,5-dicarboxylates (1) and B-allyldiisopinocampheylborane (2) to give the corresponding chiral homoallylamine with good yield in enantioselectivities up to 73% ee.*

Since several significant discoveries[1] on allyl organometallic chemistry have been made, significant synthetic interest began to emerge in the control of the stereochemistry of C-C bond formation in the reactions of various allylmetals with C=O and C=N compounds. Although a number of chiral allylmetal reagents have been developed for the highly enantioselective additions to aldehydes,[2] to our knowledge, there is no report on enantioselective addition to carbon-nitrogen double bonds.[3] Such reactions are of synthetic value because the optically active homoallylic amines formed are useful compounds for the further transformations.[4]

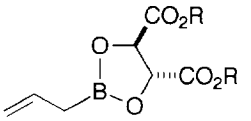
During our continuing studies on the nucleophilic additions of organometallic reagents to *N*-masked derivatives of ammonia,[5] we have found that triallylborane[6] smoothly adds to *N*-(trimethylsilyl)benzaldehyde imine. Usual aqueous workup of the reaction mixture can easily remove silyl group to give the corresponding primary homoallylamine, 1-phenyl-3-butenamine, in high chemical yield (Table 1, entry 1). This finding encouraged us to apply this reaction to asymmetric version of imine allylation. In this paper, we wish to describe the first application of chirally modified allylboron reagents to enantioselective addition to the achiral *N*-trimethylsilylimine (Scheme 1).



Scheme 1

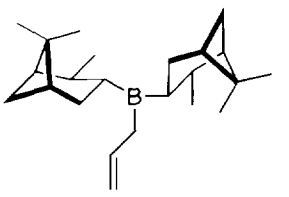
Of the wide range of chiral allylation reagents, dialkyl 2-allyl-1,3,2-dioxaborolane-4,5-dicarboxylates (**1**)[7] and *B*-allyldiisopinocampheylborane (**2**)[8] have been shown to be efficient for the enantioselective addition to carbonyl substrates. Initially, we examined the chiral allylboronate **1** for the enantioselective allylation of

the *N*-(trimethylsilyl)benzaldehyde imine. The chiral allylboronates **1**, which were originally introduced by Roush for the enantioselective allylation of aldehydes,[7] were readily obtained from homochiral tartrate esters and triallylborane. Although the reactions of imines with allylboronates having cyclic structures are generally slow and sometimes require heating,[9] the chiral allylboronate **1a** derived from dimethyl L-tartrate and triallylborane reacted with the silyl imine smoothly even at -78°C for 3 hours in THF to give the corresponding homoallylamine in 83% yield with 39% ee (entry 2). Other L-tartrate ester modified reagents used resulted in similar degree of selectivities with *R* configuration in the allylation reaction. Dialkyl tartrates were readily separated from the produced chiral homoallylamine and recovered almost quantitatively. Results are summarized in Table 1.



1

a: R=Me
b: R=Et
c: R=*i*-Pr



2

Table 1 Enantioselective Addition of Chiral Allylborane to *N*-(Trimethylsilyl)benzaldehyde Imine

Entry	Allyl organometallic	Solvent	Reaction temp. °C	1-Phenyl-3-butenamine		
				Yield,%[a]	ee,%[b]	*Confign.*[c]
1	triallylborane	THF	0	90	-	-
2	**1a**	THF	-78	89	39	*R*
3	**1b**	THF	-78	70	25	*R*
4	**1c**	THF	-78	83	32	*R*
5	**2**	THF	-78	65	64	*S*
6	**2**	ether	-78	70	73	*S*
7	**2**	ether	-30	76	43	*S*
8	**2**	ether	0	54	23	*S*

[a] Isolated yield. [b] Determined by chiral HPLC analysis. [c] The absolute configuration of the product was correlated to the known (*S*)-(-)-1-phenyl-3-butenamine. [Basile T., Bocoum, A., Savoia, D., Umani-Ronchi, A. *J. Org. Chem.*, **1994**, *59*, 7766.]

Brown developed various chiral *B*-allyldialkylboranes derived from terpenes to achieve very high enantioselectivities in the allylation of aldehydes.[8,10] Of these reagents, **2** can be easily prepared by one-pot reaction of commercially available (-)-*B*-chlorodiisopinocampheylborane [(-)-DIP-Chloride™],[11] allyl chloride, and magnesium. Thus the chiral allylborane **2** is another choice of the allylating agent for the silyl imine. We have then examined **2** for the enantioselective allylation of the silyl imine and found the improved enantioselectivity (64% ee) with **2** in THF at -78°C (entry 5). The allylation with **2** gave primary homoallylamine with *S* configuration predominantly. The use of ether as solvent gave somewhat better results in enantioselectivity to achieve 73% ee (entry 6). The enantioselectivities decreased with a rise in temperature (entries 6-8).

The following experiment is typical: To a stirred mixture of 0.44g (18 mmol) of magnesium and (-)-DIP-Chloride (3.85g, 12 mmol) in 30 ml of dry ether under nitrogen atmosphere at 0°C was added an ether solution of allyl chloride (0.92g, 12 mmol). After stirring for 1 hour at the same temperature, obtained clear solution was cooled to -78°C and an ether solution of *N*-(trimethylsilyl)benzaldehyde imine[12] (1.42g, 8 mmol) was added dropwise. The reaction mixture was stirred for 3 hours at -78°C and quenched by addition of 2M HCl. The aqueous layer was separated, washed with ether, neutralized with NH_4OH, and extracted with ether. The combined extracts were dried on $MgSO_4$ and concentrated by rotary evaporation yielding a colorless oil (0.82g, 70%) which is essentially pure 1-phenyl-3-butenamine. The product was purified by bulb-to-bulb distillation (70°C/1 mmHg). ^{1}H-NMR (270 MHz, CDCl3) δ 7.34-7.22 (m, 5H), 5.82-5.68 (m, 1H), 5.15-5.06 (m, 2H), 3.98 (dd, 1H, *J*=7.81 and 5.37 Hz), 2.46-2.32 (m, 2H), 1.53 (br, s). The enantioselectivity 73% ee was determined by chiral HPLC analysis {Daicel Chiralcel OD or OD-H, hexane-isopropyl alcohol-diethylamine (90 : 10 : 0.1)}.

In conclusion, *N*-(trimethylsilyl)benzaldehyde imine was enantioselectively allylated with chirally modified allylborane reagents to give chiral primary homoallylamine in good yield with high enantioselectivity. This is the one of the most convenient methods to obtain chiral primary homoallylamine. Further investigation for the various chiral allylation reagents of imines including other *N*-metalloimines is now in progress.

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