Axially Chiral Allenylboranes: Catalytic Asymmetric Synthesis by Palladium-catalysed Hydroboration of But-1-en-3-ynes and their Reaction with an Aldehyde

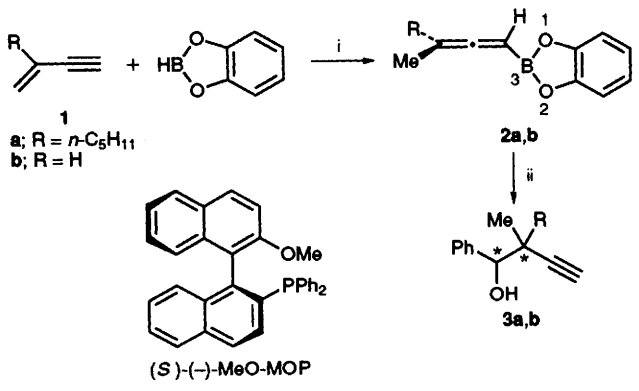
Yonetatsu Matsumoto, Masaki Naito, Yasuhiro Uozumi and Tamio Hayashi*

Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo 060, Japan

Reaction of but-1-en-3-ynes (CH_2=CR–C≡CH: R = H, *n*-C_5H_{11}) with catecholborane in the presence of a palladium catalyst bearing a chiral monodentate phosphine ligand, (*S*)-(−)-MeO-MOP, give optically active (3-substituted-1,2-butadienyl)-1,3,2-benzodioxaborolanes [Me(R)C=C=CH($BO_2C_6H_4$)], the reaction of which with benzaldehyde proceeded with *syn* attack to give the corresponding optically active but-3-ynyl alcohols of up to 61% enantiomeric excess (e.e.).

Optically active allenylboranes are useful chiral propynylating agents reacting with aldehydes in a regiospecific manner with asymmetric induction.[1] However, no optically active allenylboranes whose chirality is due to the allene axial chirality have been reported so far. The axial chirality of optically active allenylboranes is expected to be transferred to the carbon central chirality of the products in the reaction with prochiral carbonyl compounds and the stereochemical results will provide significant information on the mechanism of the $S_{E'}$ reaction. We have previously reported the palladium-catalysed hydroboration of 1,3-enynes producing allenylboranes.[2] Here we describe the application of the catalytic hydroboration to asymmetric synthesis of axially chiral allenylboranes and their reaction with an aldehyde.

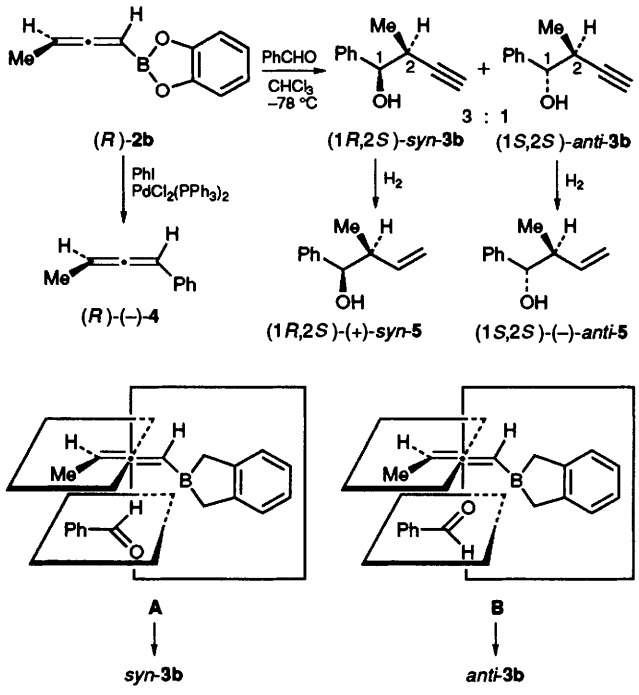
Optically active allenylboranes **2**, which have axial chirality, were obtained by the palladium-catalysed hydroboration using (*S*)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl [(*S*)-(−)-MeO-MOP][3] as a chiral phosphine ligand (Scheme 1). Reaction of 2-pentylbut-1-en-3-yne **1a** with catecholborane at 20 °C for 1.5 h in the presence of 1 mol% of a palladium catalyst generated from $Pd_2(dba)_3$·$CHCl_3$ (dba = dibenzylideneacetone) and (*S*)-(−)-MeO-MOP (Pd/P = 1/1) gave 56% yield of a mixture of (3-pentylbuta-1,2-dienyl)-1,3,2-benzodioxaborolane **2a**[2] and (3-pentylbuta-1,3-dienyl)-1,3,2-benzodioxaborolane[2] in a ratio of 88 : 12. The mixture, which has a negative optical rotation ($[\alpha]_D^{20}$ −18.0 (*c* 1.4, chloroform), was allowed to react with benzaldehyde at −78 °C to give optically active 2-methyl-2-pentyl-1-phenylbut-3-yn-1-ol **3a** in 42% yield based on the enyne **1a**. The but-3-ynyl alcohol **3a** was found to consist of *syn* and *anti* isomers in a 1 : 1 ratio, and both of the isomers were 24% e.e., which was determined by HPLC analysis of their 3,5-dinitrophenylcarbamate esters with a chiral stationary phase column (Sumichiral OA-4100, hexane–1,2-dichloroethane–ethanol = 50/15/1). The enantioselectivity of the catalytic asymmetric hydroboration of **1a** was improved by lowering the reaction temperature to −30 °C, treatment of the resulting allenylborane **2a** with benzaldehyde giving alcohol **3a** (*syn*/*anti* = 1/1) of 40% e.e. in 17% yield based on **1a**. It follows that the e.e. of the allenylborane **2a** is at least 40%.



Scheme 1 *Reagents and conditions*: i, $Pd_2(dba)_3$·$CHCl_3$, (*S*)-(−)-MeO-MOP, $CHCl_3$; ii, PhCHO, −78 °C

The stereochemistry of the $S_{E'}$ reaction of the allenylborane with aldehyde was examined in the reaction of (1,2-butadienyl)-1,3,2-benzodioxaborolane **2b**†, which was obtained by the asymmetric hydroboration of but-1-en-3-yne **1b**. The enantioselectivity in the hydroboration was not less than 61% at −30 °C and 37% at 20 °C, which was estimated from the enantiomeric purity of the but-3-ynyl alcohol **3b** (*vide infra*). The cross-coupling reaction of allenylborane **2b**, obtained in 18% yield by the hydroboration of **1b** at 20 °C, with iodobenzene in the presence of $PdCl_2(PPh_3)_2$ gave 24% yield of known[4] (*R*)-1-phenylbuta-1,2-diene **4** ($[\alpha]_D^{21}$ −21 (*c* 0.1, acetone), 9–11% optical purity), demonstrating that the allenylborane **2b** has (*R*) configuration because the palladium-catalysed cross-coupling of alkenylboranes with aryl halides

† **2b**: ^{1}H NMR (C_6D_6) δ 1.44 (dd, *J* 7.3, 3.8 Hz, 3 H), 4.95 (dq, *J* 7.3, 7.1 Hz, 1 H), 5.26 (dq, *J* 7.1, 3.8 Hz, 1 H), 6.72–6.81 (m, 2 H), 6.87–6.95 (m, 2 H).



Scheme 2

has been reported to proceed with retention of configuration at sp^2 carbon bonded to boron.[5] The reaction of allenylborane *R*-**2b** with benzaldehyde at −78 °C in chloroform gave 43% yield of *syn*-2-methyl-1-phenylbut-3-yn-1-ol (*syn*-**3b**)‡ {34% e.e., $[\alpha]_D^{20}$ +12.0 (*c* 1.0, chloroform)} and 14% yield of *anti*-**3b**§ {37% e.e., $[\alpha]_D^{20}$ −18.9 (*c* 0.5, chloroform)} (Scheme 2). The hydrogenation of *syn*-**3b** and *anti*-**3b** in the presence of the Lindlar catalyst gave known homoallyl alcohols,[6] (1*R*,2*S*)-*syn*-**5** {34% e.e., $[\alpha]_D^{25}$ +8.1 (*c* 1.0, chloroform)} and (1*S*,2*S*)-*anti*-**5** {37% e.e., $[\alpha]_D^{25}$ −32 (*c* 0.1, chloroform)}, respectively. The enantiomeric purities of **3b** and **5** were determined by the HPLC analysis (Sumichiral OA-1000) of their 3,5-dinitrophenylcarbamate esters. The *S* configuration at 2 position of both *syn*-**3b** and *anti*-**3b** clearly demonstrates that the γ carbon of allenylborane **2b** attacked the aldehyde on the same side as the boryl group (*syn* attack).[7] The *syn* attack suggests that the reaction of allenylborane with aldehyde proceeds *via* a cyclic transition state, which has been previously proposed.[1,8] It is probable that the alcohols, *syn*-**3b** and *anti*-**3b**, are formed *via* cyclic transition states **A** and **B**, respectively. The preferential formation of *syn*-**3b** over *anti*-**3b** is consistent with the rule proposed by Seebach and Golinski.[9]

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‡ *syn*-**3b**: ^{1}H NMR ($CDCl_3$) δ 1.14 (d, *J* 7.0 Hz, 3 H), 2.13 (d, *J* 2.4 Hz, 1 H), 2.19 (d, *J* 3.4 Hz, 1 H), 2.85 (ddq, *J* 7.0, 5.2, 2.4 Hz, 1 H), 4.76 (dd, *J* 5.2, 3.4 Hz, 1 H), 7.16–7.50 (m, 5 H).

§ *anti*-**3b**: ^{1}H NMR ($CDCl_3$) δ 1.12 (d, *J* 6.7 Hz, 3 H), 2.22 (d, *J* 2.4 Hz, 1 H), 2.50 (d, *J* 3.7 Hz, 1 H), 2.81 (ddq, *J* 6.7, 4.6, 2.4 Hz, 1 H), 4.52 (dd, *J* 4.6, 3.7 Hz, 1 H), 7.23–7.47 (m, 5 H).

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