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A New Allylboronate Reagent from Pantolactone

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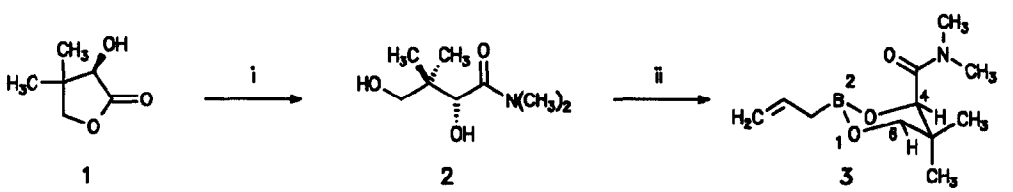
Abstract: A new enantiomerically pure six membered cyclic allylboronate **3** has been prepared from pantolactone **1**. The enantioselectivity of the allylboration was investigated on the reaction of **3** with benzaldehyde **4a** and decanal **4b**.

The allylboration reaction is a valuable method for the stereoselective preparation of carbon chains. Enantiomerically pure allylboron reagents possess particular importance for the synthesis of homochiral structures. Cyclic allylboronates[1a], modified with optically active tartaric acid derivatives[1b,c], 1,3,2-oxazaborolidines[1d], 1,3,2-diazaborolidines[1e] and several allyl dialkyl boranes[1f,g,h] have been used to produce enantiomerically pure compounds. As shown by HOFFMANN[1a] and ROUSH[1b,c] five membered cyclic 1,3,2-dioxaborolanes prepared from homochiral 1,2 diol ligands proved to be successful reagents for asymmetric allylboration.

Since five membered rings are conformationally flexible it was our aim to decrease this flexibility by preparing conformationally more rigid six membered cyclic 1,3,2-dioxaborinanes. An enantiomerically pure bidendate ligand **2** for the boron could be obtained by ring opening of D(-)2-hydroxy-3,3-dimethyl-γ-butyrolactone [D(-)pantolactone] **1** in almost quantitative yield[2,3]. The enantiomeric purity (ee > 99 %) of the amide **2** was determined on the dibenzoate derivative of **2** by chiral phase HPLC (Nucleosil Chiral 2®).



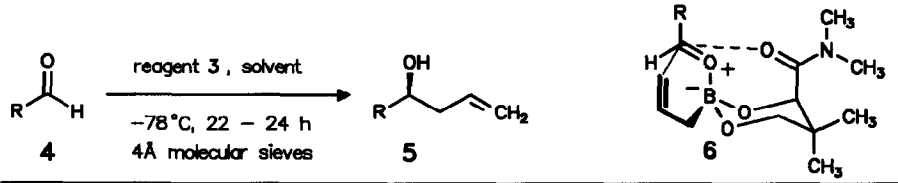
Scheme I: (i) $HN(CH_3)_2$, EtOH (98%); (ii) allylboronic acid, ether (98%)

The homochiral ligand **2** yields the crystalline 1,3,2-dioxaborinane **3** on treatment with allylboronic acid[1b,4]. The ^{1}H-NMR spectrum of **3** shows a ^4J-w-coupling between the hydrogen atoms in position 4 and 6. From the equatorial position of the 4H atom follows the axial arrangement of the amide group and the expected rigid conformation of **3**.

Reaction of the allylboronate **3** with aldehydes **4a** and **4b** in dichloromethane or toluene yields the corresponding adducts **5a** and **5b**. The preferential attack of the boronate onto the Si-face of the aldehydes could be explained by the transition structure **6**. The aldehyde becomes axially coordinated to the boron atom

and the amide oxygen lone pair interacts with the aldehyde carbonyl group thus favouring the transition state and shielding the Re-face[5]. The applicability of boron reagents derived from pantoamides in other reactions are currently under investigation.

Table I: Allylboration of aldehydes with 3 and proposed transition state 6



entry	aldehyde	solvent	product	% yield[a]	% ee [config.][c]
1	benzaldehyde **4a**	CH_2Cl_2	**5a**	76	59 [S][d]
2	benzaldehyde **4a**	toluene	**5a**	82	37 [S][d]
3	decanal **4b**	CH_2Cl_2	**5b**	36[b]	47 [R][e]
4	decanal **4b**	toluene	**5b**	29[b]	28 [R][e]

[a]Yield after purification by chromatography. [b]Reactions were worked up after 24 h and found to be not completed. [c]Absolute configurations of the products were assigned by comparision with the products described in [1b]. [d]Enantiomeric excesses were determined on the benzoate derivatives by chiral phase HPLC with Nucleosil Chiral 2®, n-heptane/isopropanol/TFA= 100/0.4/0.04. [e]Enantiomeric excesses were determined by ^{1}H-NMR of the [R]-MTPA ester.[6]

References and Notes

1a) Hoffmann, R.W.; Herold, T. *Chem. Ber.* **1981**, *114*, 375; **1b)** Roush, W.R.; Walts, A.E.; Hoong, L.K. *J. Am. Chem. Soc.* **1985**, *107*, 8186; **1c)** Roush, W.R.; Banfi, L. *J. Am. Chem. Soc.* **1988**, *110*, 3979; **1d)** Reetz, M.T.; Zierke, T. *Chem. Ind.* **1988**, 663; **1e)** Corey, E.J.; Yu, C.M.; Kim, S.S. *J. Am. Chem. Soc* **1989**, *111*, 5495; **1f)** Brown, H.C. ; Randad, R.S.; Bhat, K.S.; Zaidlewicz, M. Racherla, U.S. *ibid.* **1990**, *112*, 2389; **1g)** Garcia, J.; Kim, B.M.; Masamune, S. *J. Org. Chem.* **1987**, *52*, 4831; **1h)** Short, R.P.; Masamune, S. *J. Am. Chem. Soc.* **1989**, *111*, 1892.

2) **D(-)2R,4-Dihydroxy-3,3-dimethyl-N,N-dimethyl-butyramide (2)**: 7.0 g (53.8 mmol) D(-)2-Hydroxy-3,3-dimethyl-γ-butyrolactone **1** was added to 100 ml ethanolic solution of dimethyl amine (33%) and stirred for three days in an open reaction flask so that the solvent was allowed to evaporate. The crude product was dried and purified by chromatography and recrystallization from ether. Yield: 9.22 g (52.6 mmol, 98%) **2**. - m.p. 58°C.- $[\alpha]^{20}_D$ = -88±2 (c = 1 in CH_2Cl_2).- ^{1}H-NMR ($CDCl_3$): δ = 0.93 (s, 3H,-CH_3), 0.98 (s, 3H,-CH_3), 3.03 (s, 3H,-NCH_3), 3.10 (s, 3H,-NCH_3), 3.42 (d, *J* = 12 Hz, 1H, γ-H), 3.58 (d, *J* = 12 Hz, 1H, γ-H), 4.45 (s, 1H, α-H).- MS (70eV): m/z (%) = 175 (0.25) [M^+], 103 (100) [M^+-$CON(CH_3)_2$].- IR (KBr): 3400 cm^{-1}, 1605.- Anal. calcd for $C_8H_{17}NO_3$ (175.23): C 54.84; H 9.78; N 7.99. Found: C 54.67; H 9.65; N 7.91.- The enantiomeric excess of **2** was determined by chiral phase HPLC on the dibenzoate derivative (Nucleosil Chiral 2 ®, Macherey-Nagel), n-heptane/1,4-dioxane = 70/30, 1 ml/min, retention time 6 min (rac-**2**: 6 and 6.7 min), UV 254 nm, ee > 99%.

3) For the preparation of the primary amide see: Parke, H. C.; Lawson, E. J. *J. Am. Chem. Soc.* **1941**, *63*, 2869.

4) **2-Allyl-5,5-dimethyl-1,3,2-dioxaborinane-4R-N,N-dimethyl-carboxamide (3)**: 1.0 g (5.71 mmol) **2** was dissolved in 25 ml ether and added to 25 ml of a 0.5 M solution of allylboronic acid[1b] in ether. 3Å molecular sieves was added and the mixture was stirred under argon at 25°C for 21 hours. After filtration the solvent was evaporated and crystalline product was obtained by Kugelrohr distillation (110-120°C, 0.1 Torr). Yield 1.26 g (5.60 mmol, 98%) **3**. - m.p. 39°C.- $[\alpha]^{20}_D$ = -140±2 (c = 1 in CH_2Cl_2).- ^{1}H-NMR ($CDCl_3$): δ = 0.88 (s, 3H,-CH_3), 1.14 (s, 3H,-CH_3), 1.73 (d, J = 7.5 Hz, 2H, allyl-CH_2-), 2.98 (s, 3H,-NCH_3), 3.08 (s, 3H,-NCH_3), 3.38 (dd, ^2J = 12 Hz, ^4J = 1.5 Hz, 1H, 6-H), 4.00 (d, ^2J = 12 Hz, 1H, 6-H), 4.53 (d, ^4J = 1.5 Hz, 1H, 4-H), 4.86 - 4.99 (m, 2H, allyl=CH_2), 5.83 - 5.95 (m, 1H, allyl-CH=).- ^{11}B-NMR ($CDCl_3$): δ = 30.- MS (70eV): m/z (%) = 225 (2.5) [M^+], 184 (100) [M^+-CH_2-CH=CH_2].- IR (KBr): 2950 cm^{-1}, 1630 .- Anal. calcd for $C_{11}H_{20}BNO_3$ (225.09): C 58.70, H 8.96, B 4.80, N 6.22; Found: C 58.79, H 9.01, B 4.73, N 6.22.-

5) Roush, W. R.; Ratz, A. M.; Jablonowski, J. A. *J. Org. Chem.* **1992**, *57*, 2047.

6) Dale, J. A.; Dull, D. L.; Mosher, H. S. *ibid.* **1969**, *34*, 2543.