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Arabinose as a Chiral Auxiliary for the Asymmetric α-Hydroxyallylation of Aldehydes to *syn*-1,2-Diols

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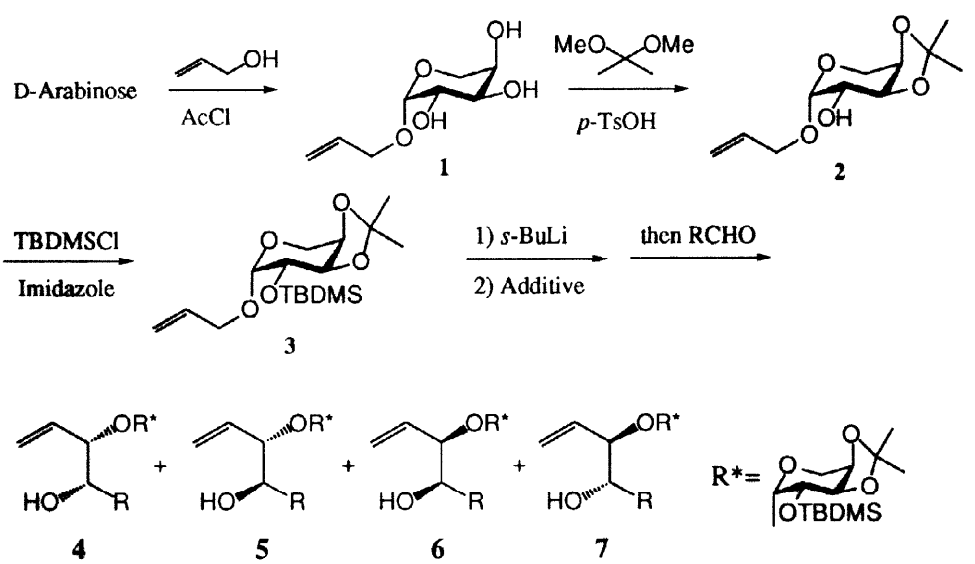
Abstract: In the presence of triethylaluminum, enantiomerically pure *syn*-1-substituted-3-butene-1,2-diol derivatives **4** are synthesized stereoselectively starting from allyl arabinopyranoside **3** and aldehydes.

The chiral 1,2-diol moiety is a common functional unit in natural products. Considerable success has been realized in the asymmetric synthesis of *syn*-1,2-diols *via* the addition of various γ-alkoxyallylmetal reagents to aldehydes.[1] Though γ-alkoxyallylic aluminum ate complexes exhibit high regio- and diastereoselectives in reaction with aldehydes to give the *syn*-diols predominantly,[2] to our knowledge, these complexes have not been applied to asymmetric synthesis of *syn*-diols. On the other hand, carbohydrates are often used as chiral auxiliaries in asymmetric synthesis.[3] In particular, arabinose is used widely because it is inexpensive, and both enantiomers are readily available from commercial sources. We report here an asymmetric α-hydroxyallylation of aldehydes using the allylic aluminum ate complex which contains an arabinose moiety as a chiral auxiliary.



Scheme 1

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The enantiomerically pure chiral auxiliary **3**[4] was prepared from D-arabinose in three steps as shown in Scheme 1. From screening of various additives in the addition reaction of the oxyallylanion, prepared from **3**, with benzaldehyde, it was found that the presence of trialkylaluminum resulted in high regio- and stereoselectivity[5] to afford the desired α-adduct **4**. Among the trialkylaluminums used, triethylaluminum was found to be best as shown in Table 1. A variety of aldehydes were allowed to react with the triethylaluminum ate complex, and the adducts were obtained regio- and stereoselectivity (Table 2). Aromatic aldehydes afforded the *syn* adducts with high diastereoselectivities and use of aliphatic aldehydes resulted in moderate selectivities.

Table 1. Reactions of γ-Oxyallylmetals with Benzaldehyde(R=Ph).

Entry	Additive	Total yield[a] (%)	Isomer ratio **4 : 5: 6 : 7**
1	$Ti(Oi\text{-}Pr)_4$	69	19 : 55 : 8 : 18
2	$ZnCl_2$	72	4 : 33 : 31 : 32
3	Me_3Al	59	90 : 0 : 7 : 3
4	Et_3Al	75	94 : 0 : 5 : 1
5	$i\text{-}Bu_3Al$	53	89 : 0 : 14 : 1

[a] Isolated yields of chromatographically pure compounds.

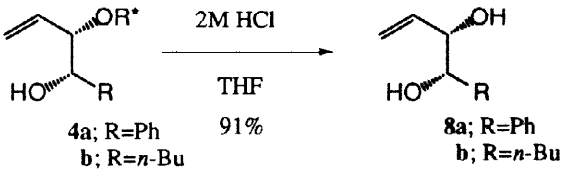
Table 2. Asymmetric Synthesis of 1,2-Diol Derivatives

Entry	RCHO	Total yield[a] (%)	Isomer ratio **4** : others
1	EtCHO	83	75 : 25
2	*i*-PrCHO	83	76 : 24
3	*n*-BuCHO	78	70 : 30
4	PhCH=CHCHO	50	81 : 19
5	$p\text{-}MeOC_6H_4CHO$	55	90 : 10
6	*p*-TolCHO	64	92 : 8
7	Ph	75	94 : 6

[a] Isolated yields of chromatographically pure compounds.

Although the diastereomers were formed in this reaction, isolation of the major product was accomplished very easily by SiO_2 flash column chromatography because of the large differences in *Rf* value between the

major isomer and others. Optically pure *syn*-diol **8** could be obtained from **4**(**a**:R = Ph, **b**:*n*-Bu) by hydrolysis using 2M HCl in 91% yield(Scheme 2). Absolute configurations of **4**(**a**:R = Ph, **b**:*n*-Bu) were determined by comparison of $[\alpha]_D$ with literature value of the derivatives.[1b, 8]



Scheme 2

Though the reaction mechanism is not fully clear, the asymmetric induction with **3** would be a consequence of the exo anomeric effect, a stereoelectronically favored conformation that places the aglycone *O*-*C* bond antiperiplaner to the pyran *C*(1)-*C*(2) bond.[1a] The aluminum ate complex apparently was formed as shown in Figure 1. It was suggested that an aldehyde should approach the *re* face of the allyl anion since the absolute configuration of the major product **4a** using benzaldehyde was *1S*, *2S*. Approach of the aldehyde to the *si* face would be blocked by the pyran *O*-*C*(5) bond.

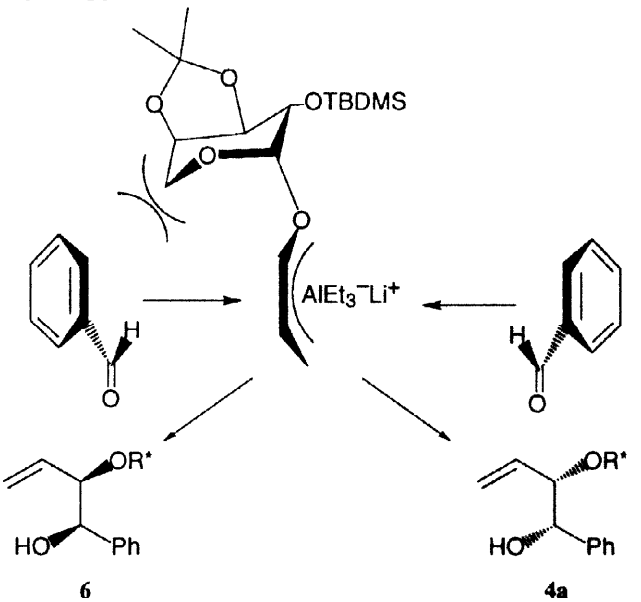


Figure 1

It should be noted that chiral *syn*-1,2-diol derivatives **4** are synthesized in good stereoselectivity with allyl arabinoside and aldehydes. Although we have reported the synthesis of one enantiomer of *syn*-1,2-diol in this paper, preparation of both enantiomers is possible by using arabinose as a chiral auxiliary.

REFERENCES AND NOTES

1. For example: (a) Roush, W.R.; VanNieuwenhze, M.S. *J. Am. Chem. Soc.* **1994**, *116*, 8536. (b) Yamamoto, Y.;Kobayashi, K.; Okano, H.; Kadota, I. *J. Org. Chem.* **1992**, *57*, 7003. (c) Sharpless, K. B.; Xu, D.; Crispino, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 7570. (d) Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1988**, *110*, 1535. (e) Wuts, P. G. M.; Bigelow, S. S. *J. Chem. Soc., Chem. Commun.* **1984**, 736. (f) Ganesh, P; Nicholas, K.M. *J. Org. Chem.* **1997**, *62*, 1737.

2. Mukaiyama, T.; Yamaguchi, M. *Chem. Lett.* **1982**, 237. (b) Koreeda, M.; Tanaka, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 845.

3. Review: Kunz, H.; Rück, K. *Angew. Chem. int. Ed. Engl.* **1993**, *32*, 336.

4. **3**: bp 120 °C (5.0 torr); $[\alpha]_D^{25} = -145.4°$ (c 1.01, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.07 (3H, s), 0.11 (3H, s), 0.89 (9H, s), 1.35 (3H, s), 1.52 (3H, s), 3.74 (1H, ddd, *J* = 1.3, 3.6, 6.9 Hz), 3.90 (1H, d, *J* = 13.5 Hz), 3.9-4.0 (2H, m), 4.1-4.2 (3H, m), 4.69 (1H, d, *J* = 3.6 Hz), 5.19 (1H, d, *J* = 10.6 Hz), 5.32 (1H, d, *J* = 17.5 Hz), 5.8-6.0 (1H, m); ^{13}C NMR (69 MHz, $CDCl_3$) δ -4.76, -4.53, 18.1, 25.8, 26.3, 28.3, 59.2, 68.6, 71.9, 73.5, 97.8, 108.6, 117.6, 133.9; Anal. Calcd for $C_{17}H_{32}O_5Si$: C, 59.27; H, 9.36. Found C, 58.77; H, 9.22.

5. Though *O*(2) of **3** was converted to other substituents (Me, $EtOCH_2CH_2$) instead of the TBDMS group, the reactions did not proceed. When *O*(2) of **3** was a free hydroxy group, the diastereoselectivity was greatly decreased (**4**:**5**:**6**:**7** = 40:11:29:20).

6. In a typical procedure, to a solution of the allyl arabinoside **3** (1 mmol) in 10 ml of tetrahydrofuran, was added *s*-butyllithium (1.4 mmol) in 1.4 ml of cyclohexane at -78 °C. After 40 min at -78 °C, the resulting carbanion was treated with triethylaluminum (1.4 mmol) in 1.5 ml of hexane at -78 °C and the temperature was maintained for another 10 min before the addition of benzaldehyde (1.0 mmol). After stirring the mixture for 2 h, the reaction was quenched with 1M NaOH. Usual work-up and purification gave the vicinal diol derivatives **4a**(R = Ph).[7]

7. **4a**: mp 68-69°C(hexane); $[\alpha]_D^{27} = -90.4°$ (c 0.98, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.18 (3H, s), 0.19 (3H, s), 0.97 (9H, s), 1.37 (3H, s), 1.55 (3H, s), 3.78 (1H, dd, *J* = 3.6, 6.9 Hz), 3.88 (1H, d, *J* = 9.6 Hz), 3.93 (1H, d, *J* = 4.6 Hz), 3.97 (1H, OH, d, *J* = 1.0 Hz), 4.11 (1H, dd, *J* = 2.6, 16.2 Hz), 4.22 (1H, dd, *J* = 6.0, 12.0 Hz), 4.23 (1H, s), 4.55 (1H, dd, *J* = 1.0, 8.9 Hz), 4.94 (1H, d, *J* = 3.3 Hz), 5.01 (1H, d, *J* = 17.3 Hz), 5.07 (1H, d, *J* = 10.6 Hz), 5.66 (1H, ddd, *J* = 7.3, 10.6, 17.8 Hz), 7.2-7.3 (5H, m); ^{13}C NMR (69 MHz, $CDCl_3$) δ -4.36, 18.3, 26.0, 26.3, 28.3, 59.6, 73.2, 73.4, 76.5, 76.6, 88.4, 101.7, 108.7, 119.0, 127.6, 128.0, 128.1, 134.5, 139.1; Anal. Calcd for $C_{24}H_{38}O_6Si$: C, 63.97; H, 8.50. Found C, 63.89; H, 8.55.

8. Diastereomerically pure **4a** and **4b** were converted to known compounds[1b] **9a** and **9b**.