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Stereoselective synthesis of vicinal diols by the stannous chloride-mediated reaction of unprotected hydroxyallylic stannane with carbonyl compounds

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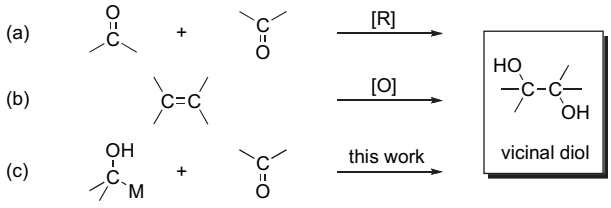
ABSTRACT

The highly stereoselective synthesis of vicinal diols was accomplished by the reaction of hydroxymethyl anion equivalents with carbonyl compounds. The reaction of hydroxyallylic stannanes with various aldehydes gave but-3-en-1,2-diols in the presence of $SnCl_2$. The diol moiety showed *syn*-diastereoselectivity. A mechanism for this reaction was proposed: transmetalation of the hydroxyallylic stannane with $SnCl_2$ gives an active rearranged allylic tin(II) species, which adds to carbonyl compounds through a cyclic transition state. The use of either α-alkoxy or hydroxy carbonyl compounds instead of aldehydes also gave the corresponding vicinal diols with high selectivity. In this case, either the alkoxy or the hydroxy group effectively coordinates to the tin(II) center to form a transition state that leads to high selectivity. The reaction of hydroxyallylic stannane with α-alkoxy aldehyde afforded the product through a cyclic transition state according to the Felkin–Anh model. This system was applied to sugar synthesis because conventional treatment of protected (*R*)-glyceraldehyde led to D-arabinose. The configurations of the major products were determined by means of X-ray structural analysis.

1. Introduction

Polyols are key compounds, and the development of methodology for their synthesis is quite important as numerous natural compounds contain this structural motif.[1] Therefore, the stereoselective synthesis of vicinal diols has been studied intensively, as shown in Scheme 1. Among relevant stereoselective reactions, the reductive coupling of carbonyls (pinacol-coupling) gives vicinal diols,[2] but cross-/homo-selectivity and stereoselectivity are often difficult to control. To overcome these limitations, alternative methods have been developed. Although oxidation of olefins is a powerful method for the synthesis of vicinal diols (Scheme 1b),[3] oxidation at sites other than the olefin moiety can interfere with the desired outcome. In this context, new regio- and stereoselective synthetic routes to 1,2-diols are still required. We hypothesized that the addition of a hydroxymethyl anion equivalent (hydroxymethylmetal species) to a carbonyl would accomplish the selective synthesis of vicinal diols because cross-selectivity is likely to occur and stereoselectivity can be controlled by metal-mediated carbonyl addition (Scheme 1c). To realize this reaction path (c), the hydroxymethylmetal must be inert to acidic OH groups, yet possess suitable reactivity.



Scheme 1. Synthetic protocols of vicinal diols.

We previously reported an allylic stannane/$SnCl_2$ system for carbonyl allylation, in which OH-substituted substrates could be used with no decomposition of the active species.[4,5] This result prompted us to prepare the allylic stannyl compound **1a** (*M*=*Sn*) as a hydroxymethyl anion equivalent (Scheme 2). The reaction between the MOM-protected form of the allylic stannane **1a**-**MOM** with carbonyl groups reportedly is mediated by Lewis acids that are not compatible with free OH groups.[6,7] The unprotected allylic stannane **1** has not been used in organic syntheses because very few reaction conditions are compatible with the free OH group.[8] Herein, we report the highly stereoselective, $SnCl_2$-mediated addition of α-hydroxyallylic stannane to carbonyl compounds.[9]

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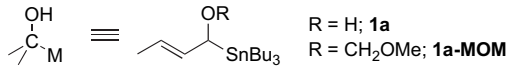
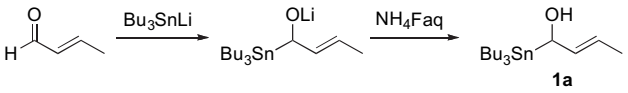


Scheme 2. Hydroxyallylic stannane **1a** as a hydroxymethyl anion equivalent.

2. Results and discussion

2.1. Generation of hydroxyallylic stannane and its reaction with benzaldehyde

Treatment of 2-butenal with Bu_3SnLi followed by aqueous quenching, extraction, and concentration gave OH-substituted allylic stannane **1a** as a crude mixture (Scheme 3). The ^1H NMR spectrum is shown in Supplementary data. Purification of the crude product by distillation failed, giving a complicated mixture. Thus, the crude product containing compound **1a** was treated with benzaldehyde **2a** in the presence of $SnCl_2$.[10] The vicinal diol **3aa** was obtained in high yield and with high diastereoselectivity (Table 1, Entry 1). The stereochemistry of the product was unambiguously determined by X-ray analysis of compound **3aa′** (described in Scheme 10), which was derived from **3aa** and found to be in the *syn* configuration. Solvents such as dichloromethane, propionitrile, and THF gave the product in high yields (Entries 1–3), while DMSO failed to give **3aa** (Entry 4). The reaction without $SnCl_2$ did not yield the desired product (Entry 5). Typical Lewis acids that are often used for allylation by allylic stannanes, such as $BF_3\cdot OEt_2$ or $TiCl_4$,[12] gave unsatisfactory results, probably because the unprotected OH groups decomposed the Lewis acids (Entries 6 and 7). $InCl_3$ that tolerates an OH group did not give the product at all (Entry 8).[13]



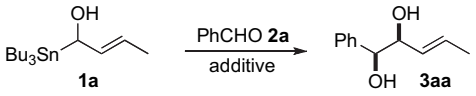
Scheme 3. Generation of hydroxyallylic stannane **1a**.

2.2. Reaction of hydroxyallylic stannanes with aldehydes

We explored the generality of this method by using various aldehydes **2**. The results of these experiments are shown in Table 2. The aromatic aldehydes **2a**–**e** gave the products in high yield and with high selectivity—even with electron-donating or -withdrawing groups (Entries 1–5). In Entry 3, the phenolic OH on substrate **2c** did not depress the reaction. The α,β-unsaturated aldehyde **2f** also afforded the diol **3af** as a result of 1,2-addition (Entry 6). Highly selective diol synthesis was also achieved using the aliphatic aldehydes **2g** and **2h** (Entries 7 and 8). The furyl group in **2i** did not affect the reaction system and gave **3ai** (Entry 9). The aldehyde **2j**, which has an olefinic moiety, afforded the corresponding product **3aj** with no change to the double bond (Entry 10). Use of **1b**, which was prepared from 2-heptenal, as the starting material also gave the product **3ba**, which has a longer carbon chain (Entry 11).[10] High diastereoselectivity was also observed in this case. The phenyl-substituted enal (2-phenyl-2-butenal)[14] generated the corresponding stannane **1c** in the *Z*-form, which reacted with **2a** to give the diol **3ca** in high yield (Entry 12).[10,11] Analysis of the stereochemistry revealed that the product was the *syn*- and *E*-form. Therefore, the stereoselectivity was independent of the olefinic geometry of the starting tin reagents. Reaction of **1c** proceeded using various types of aldehydes, including aliphatic aldehydes, to give the products in *syn*- and *E*-form in satisfactory yields (Entries 12–17). Although use of **1c** resulted in diastereoselectivities that were slightly less than those obtained using **1a** or **1b**, they were high nevertheless.

Use of an unsaturated acylstannane and methyl Grignard reagent as starting materials gave hydroxyallylic stannane **1d**, which had a quaternary carbon center, as shown in Scheme 4. Its reaction with the *p*-bromobenzaldehyde **2l** gave the corresponding vicinal diol **3dl**, which also had a quaternary carbon center, with high diastereoselectivity. The stereochemistry of the *syn*-vicinal diol moiety was confirmed by X-ray analysis.

Table 1
The reaction of hydroxyallylic stannane **1a** with benzaldehyde **3a** in the presence of $SnCl_2$[a]



Entry	Additive	Solvent	Conditions	Yield%	*syn:anti*
1	$SnCl_2$	CH_2Cl_2	rt, 5 h	84	>99:1
2	$SnCl_2$	EtCN	rt, 5 h	83	>99:1
3	$SnCl_2$	THF	rt, 5 h	84	>99:1
4	$SnCl_2$	DMSO	rt, 5 h	0	—
5	—	CH_2Cl_2	rt, 5 h	0	—
6	$BF_2\cdot OEt_2$	CH_2Cl_2	−78 °C, 3 h	0	—
7	$TiCl_4$	CH_2Cl_2	−78 °C, 3 h	12	—
8	$InCl_3$	CH_2Cl_2	rt, 3 h	0	—

[a] The reaction was carried out using α-hydroxyallylic stannane **1a** (1.0 mmol), benzaldehyde **2a** (1.0 mmol), and additive (1.0 mmol) in solvent (2 mL).

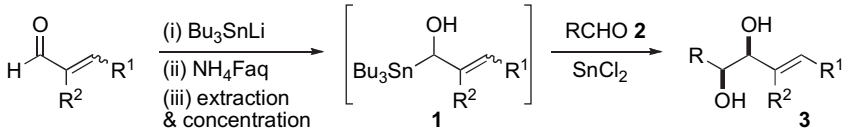
2.3. Reaction mechanism

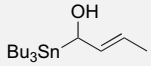
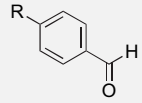
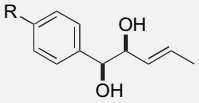
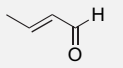
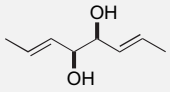
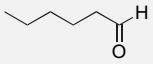
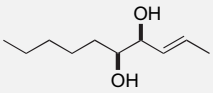
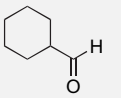
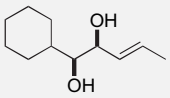
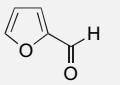
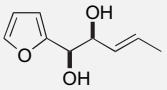
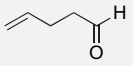
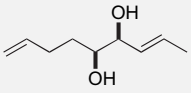
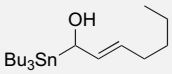
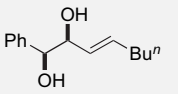
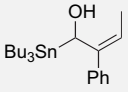
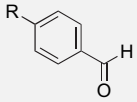
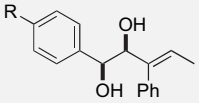
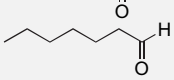
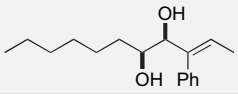
A reaction path, which is plausible based on the stereochemistry of the products, is shown in Scheme 5a. Transmetalation of hydroxyallylic stannane **1** with $SnCl_2$ gives the rearranged allylic tin species **4**-γ. The coordination of oxygen to tin(II) preferentially results in the *cis*-form of the product. The addition of the species **4**-γ to aldehyde **2** through the cyclic transition state[15] **5** gives the vicinal diol **3** with the *syn* configuration. Formation of *E*-geometry (i.e., *cis* orientation between R^1 and R^2) is ascribed to equatorial R^1 in **5**. In our previous study,[4] in which we used allylic stannane **1′** without an OH group, the γ-adduct **3′** was obtained, as shown in Scheme 5b. The generated active tin(II) species **4′**-γ rapidly rearranges to **4′**-α. By contrast, hydroxyallylic stannane **1** gives only α-adduct **3** regioselectively, without formation of the γ-adduct that forms from the tin species **4**-α. This is because the strong coordination of OH to tin(II) in **4**-γ prevents rearrangement to **4**-α. Because of its short life-time, direct observation of the intermediate **4**-γ was not possible.[16] In fact, premixing of **1a** with $SnCl_2$ for 5 min followed by the addition of benzaldehyde **2a** did not give the desired product **3aa**, but resulted in the formation of Bu_3SnCl. From these observations, carbonyl coordination to **4**-γ would be necessary to stabilize the active species **4**-γ, and the formed complex readily transforms to the allylation product. As a result, the direct observation of **4**-γ was failed in the absence of carbonyls, but the allylation products were successfully produced in the presence of carbonyls. It is interesting that the MOM-protected stannane **1a-MOM** gave lower yields and reduced selectivity compared with unprotected stannane **1a** (Scheme 6). This result suggests that the unprotected OH group induces a rigid intermediate, which leads to high yield and high selectivity.

2.4. Reaction of hydroxyallylic stannanes with α-*O*-substituted ketones

The reaction of **1a** with acetophenone, in place of aldehydes, resulted in very low yield (<5%) because of the low reactivity of simple ketones. However, the alkoxy ketone **6a** gave the desired product **7aa** in moderate yield and with excellent selectivity (Table 3, Entry 1). The reaction with the branched α-alkoxy ketone **6b** afforded

Table 2
Stereoselective synthesis of vicinal diols



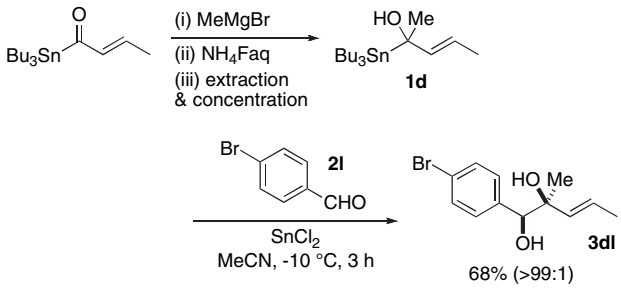
Entry	Hydroxyallylic stannane	1	Aldehyde	2	Time/h	Vicinal diol	3	Yield (%) (dr)
1[a]		**1a**		**2a** R:H	5		**3aa**	83(>99:1)[b]
2[a]		**1a**		**2b** Cl	5		**3ab**	63(>99:1)[c]
3[a]		**1a**		**2c** OH	5		**3ac**	64(>99:1)[c]
4[a]		**1a**		**2d** OMe	5		**3ad**	70(93:7)[c]
5[a]		**1a**		**2e** CO_2Me	5		**3ae**	55(95:5)[c]
6[a]		**1a**		**2f**	5		**3af**	81(91:9)[b]
7[a]		**1a**		**2g**	15		**3ag**	63(>99:1)[b]
8[a]		**1a**		**2h**	5		**3ah**	42(>99:1)[b]
9[a]		**1a**		**2i**	5		**3ai**	73(91:9)[c]
10[a]		**1a**		**2j**	5		**3aj**	86(>99:1)[c]
11[a]		**1b**		**2a**	5		**3ba**	52(>99:1)[c]
12[d]		**1c**		**2a** R:H	1		**3ca**	79(90:10)[b]
13[d]		**1c**		**2b** Cl	4		**3cb**	55(85:15)[b]
14[d]		**1c**		**2k** F	2		**3ck**	69(96:4)[b]
15[d]		**1c**		**2l** Br	4		**3cl**	75(76:24)[b]
16[d]		**1c**		**2m** Ph	1		**3cm**	69(89:11)[c]
17[d]		**1c**		**2n**	5		**3cn**	36(>99:1)[c]

[a] The reaction was carried out using **1a** (1.0 mmol), aldehyde **2** (1.0 mmol), and $SnCl_2$ (1.0 mmol) in EtCN (2 mL) at room temperature.
[b] The relative stereoconfiguration was determined based on X-ray analysis (see Scheme 10).
[c] The relative stereoconfiguration was determined by analogy.
[d] The reaction was carried out using **1c** (3.0 mmol), aldehyde **2** (1.0 mmol), and $SnCl_2$ (3.0 mmol) in MeCN (12 mL) at room temperature.

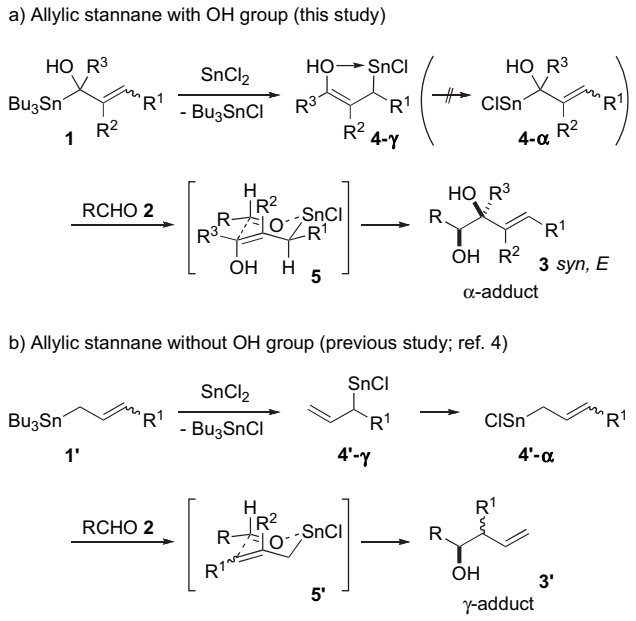
the product **7ab** as a single isomer with three sterically controlled carbons (Entry 2). The unprotected hydroxy ketone **6c** directly gave the triol **7ac** with high selectivity (Entry 3). The reaction with the α-ketoester **6d** gave the product **7ad** with moderate selectivity. The use of **1d** also gave the corresponding product with vicinal quaternary carbon centers bearing OH groups (Entry 5). The stereochemistry of the products was determined primarily by X-ray analysis (described in Scheme 10). The high selectivities were ascribed to a chelation effect of the alkoxy/hydroxy moieties in the transition state **8**, as illustrated in Scheme 7. The oxygenated substituents should occupy the axial position in the cyclic transition state to coordinate to the tin(II) center. Similarly, carbonyl coordination explains the selectivity of Entry 4 in the cyclic transition state **9**.

2.5. Reaction of hydroxyallylic stannane with α-*O*-substituted aldehyde

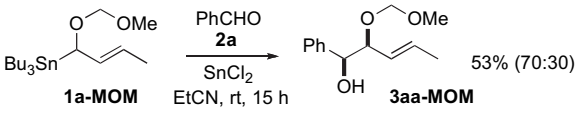
In the reaction with aldehyde described in Table 2, hydrogen occupies the axial position in the cyclic transition state owing to its smaller steric size (**5** in Scheme 5a). For α-alkoxy or hydroxy ketone, axial alkoxy/hydroxy groups stabilize the transition state by coordination to tin(II) (**8** in Scheme 7). Therefore, it would be of interest to investigate the stereoselectivity of an α-alkoxy aldehyde. The $SnCl_2$-mediated reaction of the (*R*)-glyceraldehyde derivative **10**, which is an α-alkoxy aldehyde, with **1a** gave the carbonyl adduct **11**



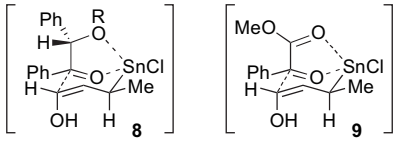
Scheme 4. Diol synthesis using an acylstannane/Grignard reagent/aldehyde system in the presence of $SnCl_2$.



Scheme 5. Plausible reaction path.

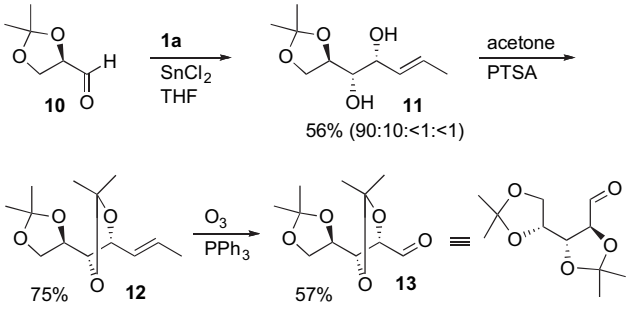


Scheme 6. Reaction of MOM-protected stannane.

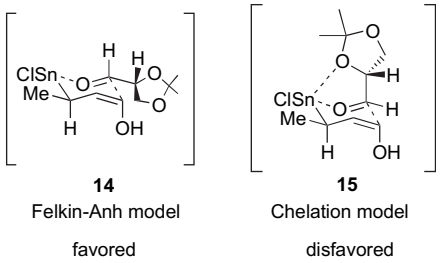


Scheme 7. Chelation-controlled transition state.

in 56% yield with a selectivity of 90:10:<1:<1 (Scheme 8). The structure of product **11** corresponded to that of D-arabinose, as confirmed by X-ray analysis of its silylated derivative **11′** (described in Scheme 10). In fact, acetonide-protection of **11** followed by ozonolysis gave the protected D-arabinose **13**. Product formation occurred via the Felkin–Anh model[17] **14** with an axial hydrogen and not via the chelation model **15** with an axial alkoxy group (Scheme 9). This result suggests that the hydroxyallylic stannane increases the C2 unit of the sugar in a stereoselective manner by a simple and short pathway.[18]



Scheme 8. Synthesis of D-arabinose derivative.

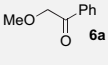
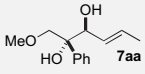
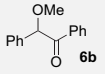
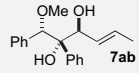
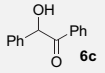
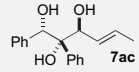
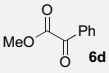
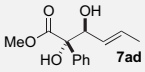
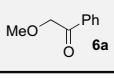
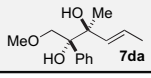


Scheme 9. Transition state for alkoxyaldehyde **10**.

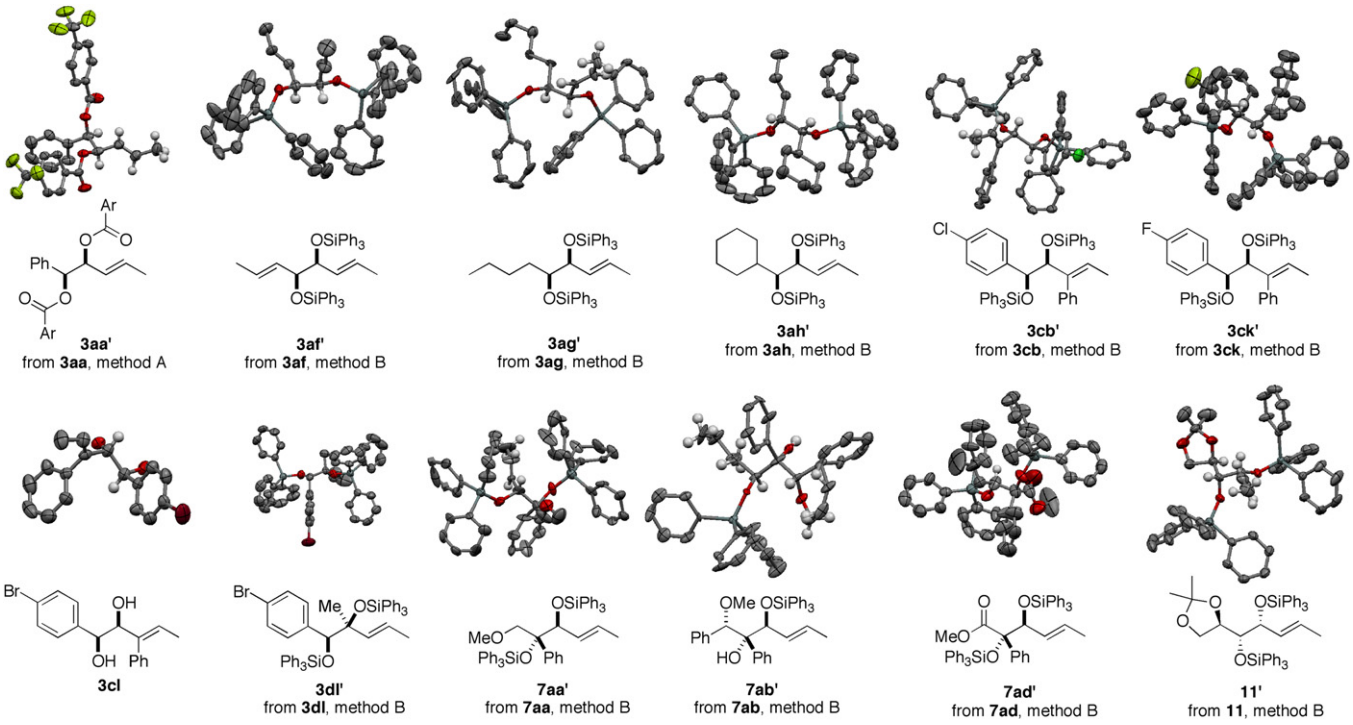
2.6. Determination of stereochemistry of the products using X-ray analysis

The stereochemistry of the formed products was determined primarily using X-ray analysis.[19] The compound **3cl** gave crystals

Table 3
Stereoselective synthesis of vicinal diols **7** derived from ketones **6**[a]

Entry	1	Ketones **6**	Conditions	Product **7**	Yield (%) (dr)
1[b]	**1a**	 **6a**	rt, 18 h	 **7aa**	52(>99:<1)[c]
2[d]	**1a**	 **6b**	rt, 5 h	 **7ab**	57(>99:<1:<1:<1)[c]
3[b]	**1a**	 **6c**	rt, 5 h	 **7ac**	40(93:7:<1:<1)[e]
4[b]	**1a**	 **6d**	rt, 5 h	 **7ad**	60(81:19)[c]
5[f]	**1d**	 **6a**	−10 °C, 3 h	 **7da**	34(>99:<1)[e]

[a] The reaction was carried out using **1** (1.0 mmol), ketone **6** (1.0 mmol), and $SnCl_2$ (1.0 mmol) in solvent.
[b] Solvent; EtCN (2 mL).
[c] The relative stereoconfiguration was determined based on X-ray analysis (see Scheme 10).
[d] Solvent; CH_2Cl_2 (2 mL).
[e] The relative stereoconfiguration was determined by analogy.
[f] Solvent; MeCN (4 mL).



Scheme 10. Determination of stereochemistry based on X-ray analysis of the product or its derivatives. Methods A: $(p\text{-}CF_3C_6H_4CO)_2O$, $MgBr_2$, Et_3N. Method B: Ph_3SiCl, imidazole.

that were suitable for analysis and the compound was determined to be in the *syn* configuration. Several other compounds were analyzed after either esterification or silylation to obtain suitable crystals. The results are summarized in the ORTEP drawings of the products shown in Scheme 10. The products resulting from the reactions using either aldehydes, *O*-substituted ketones, or *O*-substituted aldehyde were analyzed. Although X-ray analysis was not employed for all products, the analysis shown in Scheme 10 is adequate to establish the stereochemistry of this reaction system.

3. Conclusion

In summary, the reaction of hydroxyallylic stannanes with carbonyl compounds gave vicinal diols with high stereoselectivity. The unprotected OH-substituted nucleophiles were activated by transmetalation with $SnCl_2$ to generate nucleophilic tin(II) compounds bearing OH groups. The strict interaction between the unprotected hydroxy moiety and the tin(II) center accounts for the high stereoselectivity of the reaction. A wide range of carbonyl compounds was successfully applied to the synthesis of vicinal diols with high stereoselectivity. The stereochemistry of the products was determined based on X-ray analysis. Application of this reaction system to sugar synthesis was successful due to the stereoselective formation of oxygenated carbon–carbon bonds.

4. Experimental section

4.1. Preparation of α-hydroxyallylic stannane 1a–c

To a solution of diisopropylamine (6.08 g, 60 mmol) in THF (70 mL) was added *n*-BuLi (1.6 M in hexane, 42 mL, 60 mmol). The solution was stirred for 30 min at 0 °C. Bu_3SnH (17.56 g, 60 mmol) was slowly added to the solution over a period of ca. 5 min at −78 °C with stirring for 1 h at the same temperature. Then the α,β-unsaturated aldehyde (crotonaldehyde, 2-heptenal, or 2-phenylcrotonaldehyde) (60 mmol) was added slowly over a period of ca. 5 min, and the resulting mixture was stirred for 5 h at −78 °C. The reaction mixture was quenched with 200 mL of NH_4Faq (15%). The organic layer was extracted with diethyl ether (3×100 mL) and dried with $MgSO_4$. Then the solvent was removed under reduced pressure. The title compound, which was obtained in nearly ca. 70% purity (a small portion was analyzed by ^1H NMR using an internal standard), was used in the synthesis of vicinal diols without further purification. See Supplementary data for the ^1H NMR spectra.

4.2. Preparation of α-hydroxyallylic stannane 1d

To a solution of diisopropylamine (4.06 g, 40 mmol) in THF (50 mL) was added *n*-BuLi (1.6 M in hexane, 28 mL, 40 mmol). The solution was stirred for 30 min at 0 °C. Bu_3SnH (11.70 g, 40 mmol) was slowly added to the solution over a period of ca. 5 min at −78 °C with stirring for 1 h at the same temperature. Then crotonaldehyde (2.8 g, 40 mmol) was added slowly over a period of ca. 5 min and the resulting mixture was stirred for 5 h at −78 °C. To the mixture was slowly added a solution of 1,1′-(azodicarbonyl)dipiperidine (ADD) (10.1 g, 40 mmol) in THF (90 mL) at −78 °C. The mixture was warmed to 0 °C and stirred for 1 h. The reaction was quenched with 200 mL of NH_4Claq (saturated). The organic layer was extracted with diethyl ether (3×100 mL) and dried with $MgSO_4$. Then the solvent was removed under reduced pressure to give the solid. The solid was dissolved in hexane (150 mL) and filtered under N_2 to afford the crude product of 1-tributylstannyl-2-buten-1-one (13.7 g, 72% purity, 27.5 mmol).[20] Then the sample (13 mmol) in THF (39 mL) was dissolved in THF (40 mL) and kept at 0 °C. To the solution was slowly added MeMgBr (3 M in Et_2O from Aldrich, 6.5 mL, 19.5 mmol). The mixture was stirred at 0 °C for 3 h. The mixture was quenched with 100 mL of NH_4Faq (15%). The organic layer was extracted with diethyl ether (3×50 mL) and dried with $MgSO_4$. Then the solvent was removed under reduced pressure. The title compound, which was obtained in 24% yield and nearly ca. 30% purity (a small portion was analyzed by ^1H NMR using an internal standard), was

used in the synthesis of vicinal diols without further purification. See Supplementary data for the ^{1}H NMR spectra.

4.3. General experimental procedure for the synthesis of vicinal diols 3 in the reaction of hydroxyallylic stannane 1 with carbonyl compounds 2 or 6 (Tables 2 and 3, Scheme 4)

To a suspension of $SnCl_2$ (1.0 mmol) and carbonyl compound **2** or **6** (1.0–3.0 mmol) in dry propionitrile, acetonitrile, or dichloromethane was added α-hydroxyallylic stannane **1** (1.0 mmol) under nitrogen (amount of the reagents are described in the text). The mixture was stirred under the conditions described in the text. The reaction mixture was quenched by the addition of aqueous NH_4F (15%; 10 mL). The resulting white precipitate was removed by filtration and the filtrate was extracted with diethyl ether (3×10 mL). The collected organic layer was dried over $MgSO_4$ and concentrated in vacuo. See Supplementary data for details of the synthesis and characterization of individual compounds.

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Supplementary data

Experimental procedures and characterization of the products. The supplementary data associated with this article can be found in the on-line version at, doi:10.1016/j.tet.2009.09.063.

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19. CCDC 737724 (**3aa**′), 737,725 (**3af**′), 737,726 (**3ag**′), 737,727 (**3ah**′), 737,728 (**3cb**′), 737,729 (**3ck**′), 737,730 (**3cl**), 737,731 (**3dl**′), 737,732 (**7aa**′), 737,733 (**7ab**′), 737,734 (**7ad**′), and 737,735 (**11**′) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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