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Synthesis and thermal stability of secondary sugar allyltin derivatives☆

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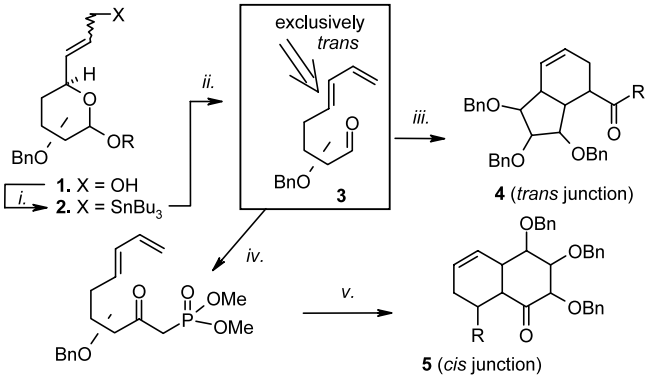
Abstract—Reaction of sugar allylic mesylates with tri-*n*-butyltin cuprate affords the primary and secondary allyltin derivatives: Sug-CH=CH-CH_2SnBu_3 and Sug-CH($SnBu_3$)-CH=CH_2 with the latter predominating. The S_N2' addition led almost exclusively to one isomer with the *S* configuration at the newly created stereogenic center. Only traces of the opposite *R* isomer were formed. Both stereoisomers of secondary allyltins decompose at high temperature (140°C) with elimination of the tin moiety and opening of the sugar ring. The main *S* isomer gives the dienoaldehyde CH_2=CH-CH=CH-[$(CHOR)_3$]-CHO with the *cis* geometry across the internal double bond. The minor *R* isomer provides the *trans* dienoaldehyde under the same conditions. These results strongly suggest the concerted (E2) mechanism of thermal decomposition of secondary sugar allyltin derivatives.

1. Introduction

Primary sugar allyltins **2** are useful starting materials for the preparation of highly oxygenated carbobicyclic derivatives.[2] They are usually prepared by a 'xanthate' method i.e. conversion of the allylic alcohol **1** into a xanthate followed by thermal [3,3] rearrangement to the thiocarbonate and radical S_R2' process with tributyltin hydride.[3] This reaction gives a mixture of the *trans*:*cis* allyltins in the ratio ~5:1 regardless of the configuration of starting allylic alcohols[4,5] (see Scheme 1). The Lewis acid induced decomposition of **2** provides the *trans*-dienoaldehydes **3** regardless of the configuration (*trans* or *cis*) of starting allyltin derivative **2**.[5,6] The diene **3** may be converted either into the *trans*-perhydroindane derivative **4**,[7] or *cis*-decalin **5** [8] (Scheme 1).

Primary allyltin derivatives may be also obtained by a nucleophilic displacement of allylic bromides with tributyltin anions in an S_N2 reaction. Very often the primary products are contaminated with the secondary isomers arising from the S_N2' reaction. Recently, we have found, that sugar allylic bromides react with tri-*n*-butyltin cuprate[9] yielding the primary **2** and secondary **6** allyltin derivatives (Fig. 1).[6] Both compounds, i.e. primary **2** and secondary **6** upon treatment with the Lewis acid afford the same *trans* dienoaldehyde **3**.[1] However, the secondary isomer (of unknown configuration at the newly created stereogenic center) decomposes thermally to the *cis*-dienoladehyde **7**.[1]



Scheme 1. *Reagents and conditions*: (i) Ref. 5: a. NaH, CS_2, MeI, b. 140°C, c. Bu_3SnH; (ii) Ref. 5: $ZnCl_2$, CH_2Cl_2, rt, 2 h; (iii) Ref. 7: Ph_3P=CH-COR, then cyclization; (iv) Ref. 8: a. [O], b. CH_2N_2, c. $^{(-)}CH_2P(O)(OMe)_2$; (v) RCHO, K_2CO_3, 18-crown-6, toluene, rt.

☆ See Ref. 1.

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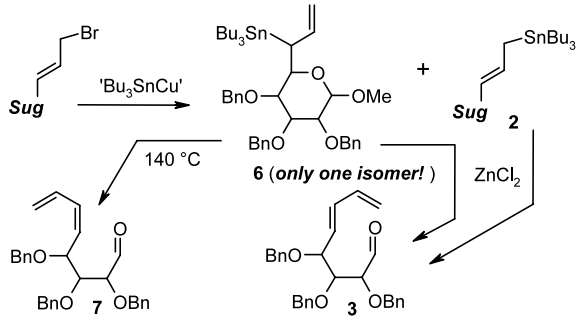


Figure 1. Reaction of sugar allylic bromides with tributyltin hydride and controlled decomposition of sugar allyltin derivatives.

Because of the usefulness of the tin methodology in stereoselective synthesis of highly oxygenated carbocyclic derivatives we decided to study in detail the preparation of sugar allyltins as well as their controlled decomposition leading to dienoladehydes such as **3**. Two interesting problems need explanation: (i) extremely high selectivity in the S_N2' reaction leading almost exclusively to one stereoisomer and (ii) determination of the configuration at the newly created stereogenic center in the S_N2' product **6**.

2. Synthesis of secondary sugar allyltin derivatives

Reaction of sugar allylic bromides with tributyltin cuprate ('Bu_3SnCu') provides a mixture of the S_N2 and S_N2' allyltin derivatives. Since the secondary derivatives are precursors of the *cis*-dienoaldehydes[1] (Fig. 1) we decided to elaborate a convenient method for effective preparation of this useful organometallic derivative. Methyl 2,3,4-tri-*O*-benzyl-α-D-*manno*-6,7-dideoxy-oct-7(*E*)-eno-pyranoside **8** (X = OH) was chosen as a model compound for this study. As nucleophiles, tributyltin cuprate ('Bu_3SnCu'),[9] tributyltin lithium (Bu_3SnLi)[10] and tributyltin sodium (Bu_3SnNa)[11] were tested. Only tributyltin cuprate reacted satisfactorily with sugar allylic derivatives; the other two compounds either did not react at all or caused decomposition of the starting material.[‡]

2.1. Model reaction of the D-*manno*-configurated allylic pyranose derivatives with tributyltin cuprate

Reaction of allylic precursors **8a**–**d** with tri-*n*-butyltin cuprate ('Bu_3SnCu'; Fig. 2) afforded the secondary allyltin derivative (*S*)-**9**[§] together with the primary one **10**. Only traces (<1%) of the alternative (*R*)-**9** isomer were isolated from the post reaction mixture (Fig. 2) The ratio of the organometallic products (primary versus secondary) depended on the nature of sugar allylic derivative (X = Cl, Br, I, OMs). In all cases various amounts of the products resulting from the transfer of the butyl group from tin organometallic to the sugar allylic derivative were also isolated **11** and **12**, respectively;[¶] the results are shown in Table 1.

It can be seen from Table 1, that the highest yields of the S_N2' product **9** are obtained when the soft tin nucleophile ('Bu_3SnCu') reacted with sugar mesylate. The lowest yields of both: primary and secondary sugar allyltin derivatives were observed for reaction of iodide **8d** with 'Bu_3SnCu'. These results may be explained by assumption that a soft nucleophile ('Bu_3SnCu') reacts preferentially with the soft center of the allylic system (Fig. 3).

2.1.1. Mechanism of the decomposition of secondary sugar allyltin derivatives: determination of their configuration. Determination of the configuration of tin derivatives is not trivial. However, the structure of the organotin compound may often be deduced from the products of their controlled decomposition[12] if the mechanism of such process is known. The most appealing one was the free radical mechanism shown in Figure 4. Homolytic cleavage of the tin–carbon bond should lead to radical **9′**, which might further decompose to **15**.

This reaction requires a cleavage of the carbon–oxygen bond under radical conditions; such processes, although not common, are known.[13] To check if radicals are involved in decomposition of secondary sugar allyltin derivatives, compound **9** was heated at 140°C in the presence of Bu_3SnH and separately $(Bu_3Sn)_2$. ***No formation*** of either a reduced compound **9″** or a primary (*Z* or *E*) allylstannane **10** (which is stable up to at least 170°C) was noted, which excludes the radical mechanism of decomposition.

However, if the concerted (E-2) mechanism is postulated, the high stereoselectivity of the decomposition is readily explained (Fig. 5). Also, according to this E-2 mechanism the configuration at the newly created stereogenic center (C-6) in **9** could be easily determined from the geometry of the decomposition products (Fig. 5).

The main isomer of **9** decomposed at high temperature (140°C) with elimination of the tributyltin moiety and opening of the sugar ring. The configuration across the internal double bond in the product of the controlled decomposition of the main isomer of **9**—the dienoaldehyde **15**—was assigned as *Z*.[14] Assuming the antiperiplanar arrangement of both leaving groups ($SnBu_3$ and the ring oxygen atom; **13** in Figure 5) the

[‡] Both stannyl-metal compounds (Bu_3SnLi and Bu_3SnNa), however, reacted with sugar aldehydes to afford known carbinols.[6]

[§] For determination of the configuration of compounds **9**, see Section 2.1.1.

[¶] The configuration at the C-6 center in **11** is assumed to be as in (*S*)-**9** on the basis of the model presented in Fig. 5.

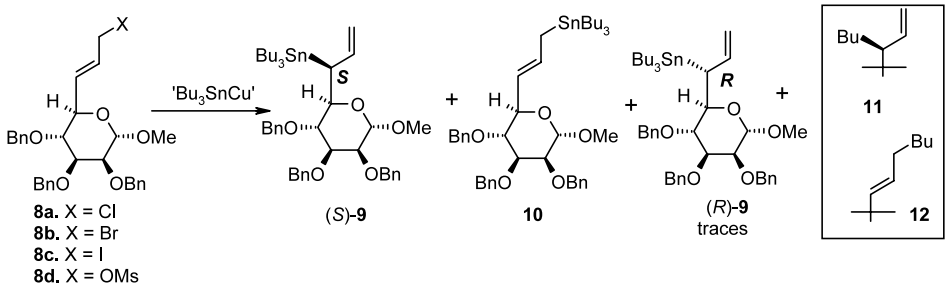


Figure 2. Reaction of sugar allylic derivatives with metallated tributyltin reagents.

Table 1. Reaction of 'Bu_3SnCu' with allylic sugar derivatives **8**

Entry	Compound	Products of the reaction (%)					
		(*S*)-**9**	(*R*)-**9**	**10**	Σ (**9**+**10**)	**11**	**12**
1	**8a** (X=Cl)[a]	39	–	38	77	0	0
2	**8a** (X=Cl)[b]	50	–	2	52	16	0
3	**8b** (X=Br)[a]	30	Traces	16	46	6.6	4
4	**8c** (X=I)[a]	14	–	11.5	25.5	2	6
5	**8c** (X=I)[b]	18	–	20	38	12	3.7
6	**8d** (X=OMs)[a]	48	–	4.6	52.6	26	0
7	**8d** (X=OMs)[b]	57	–	2.5	59.5	34	0

[a] 'Bu_3SnCu' was generated for 30 min at −78°C.
[b] 'Bu_3SnCu' was generated for 90 min at −82°C.

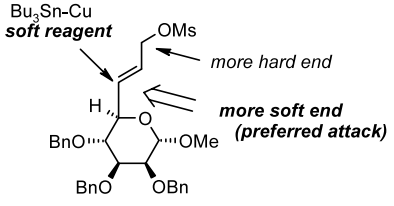


Figure 3. Regioselectivity of formation of sugar allyltins.

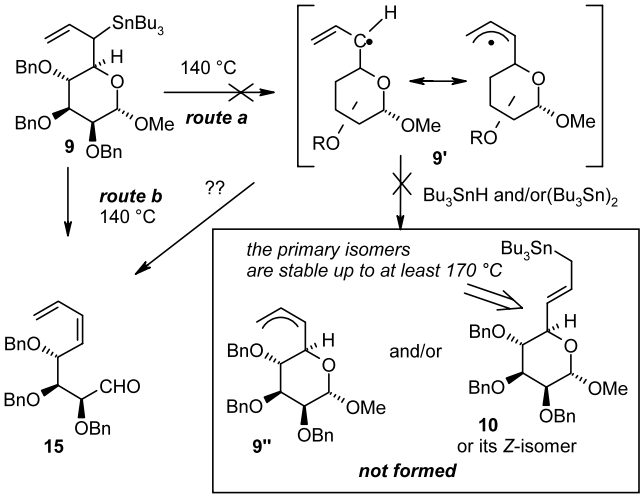


Figure 4. The (excluded) radical mechanism of decomposition of **9**.

configuration of the main isomer **9** could be assigned as (6*S*). Consequently, the opposite isomer of **9** should have the (*R*) configuration at the C-6 center and should decompose to the *trans* dienoaldehyde **16** (via **14**).

This hypothesis could be proved only, if the minor product (*R*)-**9** decomposes to the product having the opposite *E*-configuration across the C6–C7 double bond—the dienoaldehyde **16**. This diene is already known and can be prepared by a Lewis acid induced decomposition of the primary allyltin derivative **10**.[5] The problem of detection of the diene **16** in the post-reaction mixture obtained after thermal decomposition of **9** was not, however, easy. The amount of the minor secondary isomer (*R*)-**9** was very limited (less than 1%; see Table 1) and this product could not be isolated in pure form even by HPLC.

We performed, therefore, the decomposition experiment on the mixture of **9** highly enriched with the minor isomer (*R*)-**9** (*S*:*R* ratio ca. 1:1). Heating of this equimolar mixture in boiling xylene in the presence of the simplest stabilized ylide: $Ph_3P{=}CH{-}CO_2Me$ afforded two trienes differing in the configuration across the internal double bond: **17** (from **15**) and **18** (from **16**). We have already demonstrated that cyclization of such trienes is highly selective; from the *cis*-triene **17** the *cis*-perhydroindane **19** is formed,[14] while the *trans*-isomer **18** provides the bicyclic derivative **20** with the *trans* junction of the rings.[7]

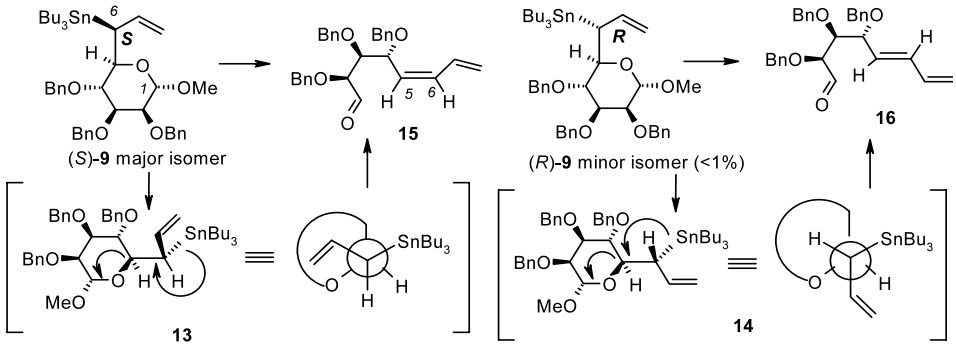
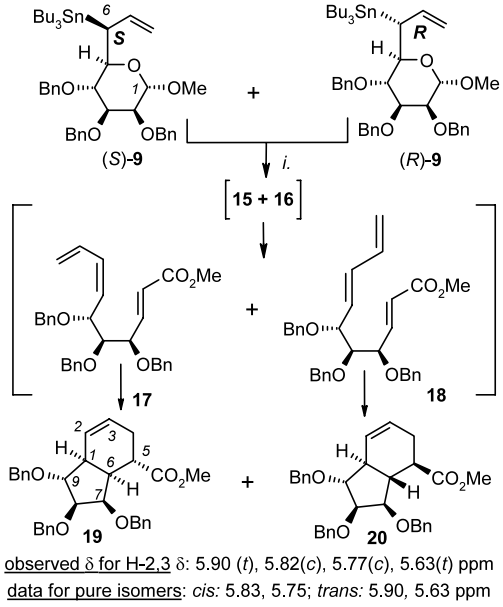


Figure 5. Stereochemical models for the controlled decomposition of secondary sugar allyltin derivatives.

The high temperature experiment conducted on a mixture of **9** in the presence of the ylide, yielded a mixture in which compounds **19** and **20** could be easily analyzed by ^{1}H NMR spectroscopy (Scheme 2). The olefinic signals (H-2,3) in the spectrum of the mixture at δ 5.90 and 5.63 ppm indicated at the structure **20**,[7] while signals at δ 5.83 and 5.75 ppm revealed the presence of the *cis* derivative **19**.[14]

The conclusion resulting from this model experiment is, that decomposition of secondary sugar allyltin derivatives proceeds via a concerted E-2 mechanism, i.e. the tributyltin moiety and the ring oxygen atom must be arranged in the antiperiplanar relationship.

The optimized conditions were applied for the effective preparation of the secondary allyltin derivatives of D-glucose (Fig. 6). Standard conditions (−78°C, 30 min)[6] afforded almost equimolar amounts of the primary and secondary allyltins **22** and **23**, while under the optimized conditions (−82°C, 90 min generation of 'Bu_3SnCu') the secondary isomer strongly predominated (ratio **22**:**23** = 1:2).



Scheme 2. *Reagents and conditions*: (i) $Ph_3P{=}CH\text{-}CO_2Me$, 140°C, xylene, 2 h.

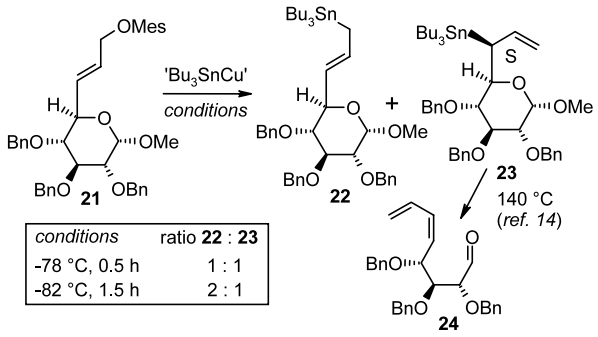


Figure 6. Reaction of **21** with 'Bu_3SnCu'.

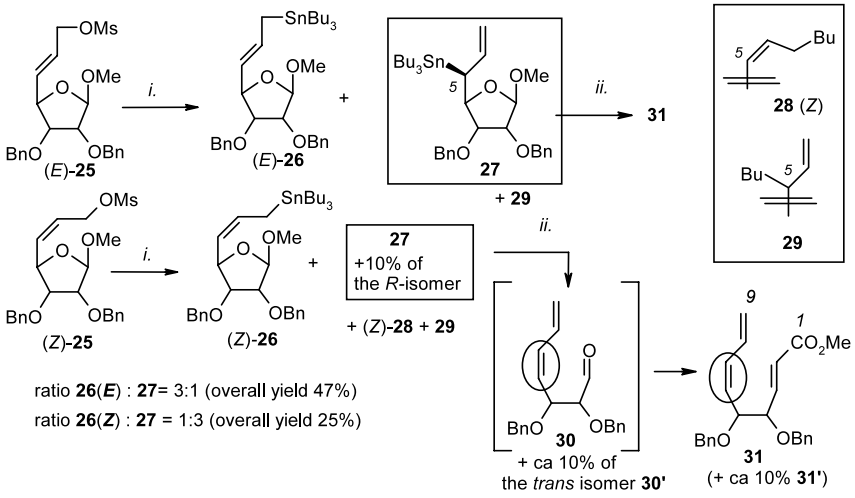
The configuration of **23** was assigned similarly to (*S*)-**9**, i.e. by thermal degradation to the *cis*-aldehyde **24**.[14]

2.2. Reaction of the allylic furanose derivatives with tributyltin cuprate

The furanose derivatives also react with 'Bu_3SnCu' in a similar way. Methyl 2,3-di-*O*-benzyl-5,6-dideoxy-β-D-*ribo*-1,4-furanos-5-ene-heptose with the *E*-configuration across the double bond (*E*)-**25** upon treatment with 'Bu_3SnCu' gave the primary allyltin (*E*)-**26** together with the secondary one **27** as a single stereoisomer. The same reaction performed for the *cis*-isomer (*Z*)-**25** gave the primary allyltin (*Z*)-**26** and ***the same*** secondary allyltin derivative **27** (Scheme 3), contaminated with traces (ca. 3%) of the opposite (*R*)-isomer. In both reactions the butylated products **28** and **29** were also formed.

Thermal decomposition of pure **27** afforded the *cis* dienoaldehyde (characterized as triene **31**), which—assuming the concerted mechanism of this elimination—strongly points to the (*S*)-configuration at the newly created stereogenic center. The same sequence of reactions performed for the sample obtained from (*Z*)-**26** afforded also **31** containing traces of the *trans* isomer (see Section 5).

This result confirmed our earlier findings (Scheme 2), that the secondary (*S*)-allyltins provide *cis*-dienoaldehydes, whilst thermal decomposition of the (*R*)-isomers leads to the *trans*-dienes.



Scheme 3. *Reagents and conditions*: (i) THF, –82°C, 'Bu_3SnCu'; (ii) xylene, 120°C, $Ph_3P{=}CH\text{-}CO_2Me$, 8 h.

The yield of allyltin derivatives was much higher for the *trans*-mesylate (*E*)-**25** than for the *cis* one. Regioselectivities in both reactions were different; for the *trans*-mesylate (*E*)-**25** the primary allyltin **26** predominated, while for the *cis* one the main isomer was the secondary derivative **27**. It is very important to note that configuration at the C-5 center is independent on the geometry of the double bond (*E* or *Z*) of starting mesylate **25**.

3. Stereochemical models for the S_N2' reaction of primary allylic sugar derivatives with 'Bu_3SnCu'

The very high stereoselectivity of the S_N2' substitution of allylic sugar derivatives with tin anions may be explained only if the fixed conformation will be assumed. The copper atom is bound to the ring oxygen atom and the X-group (mesylate, halogen) which leads either to intermediate **A-I** or **A-II** (Fig. 7). Structure **A-I** is favored over the alternative, because in the latter there are unfavorable steric interactions. Transfer of the tributyltin moiety from the reagent occurs, therefore, from the *si*-side producing the (*S*)-**9** isomer exclusively (Fig. 7).

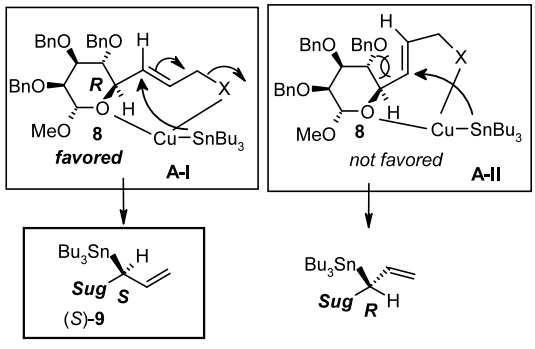


Figure 7. Stereochemical models for the S_N2' substitution of allylic sugar derivatives with tributyltin cuprate.

This model can also explain why the configuration at the newly created stereogenic center does not depend on the geometry (*trans* or *cis*) of the starting olefin. Complexation of (*E*)-**25** and (*Z*)-**25** occurs from the same side (**B-I** and **B-II** in Figure 8, respectively) and induced the attack from the *si*-side.

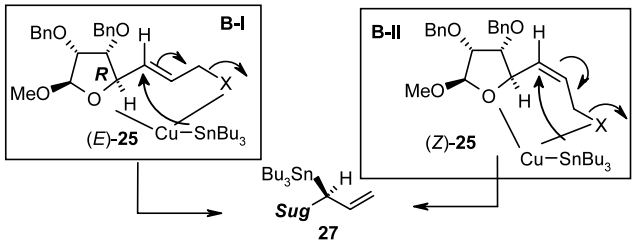
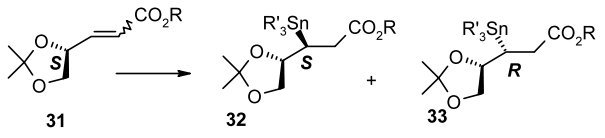


Figure 8. Stereochemical models for the S_N2' substitution of geometrical isomers of allylic sugar derivatives with tributyltin cuprate.

The results obtained by us are consistent with those reported by Krief et. al.[12] for the 1,4-addition of soft tin nucleophiles to α,β-unsaturated sugar ester **31** (see Fig. 9). Reaction of this ester derivative of D-glyceraldehyde (with the opposite to **8**, **21** and **25** configuration at the C-α to the reaction center) with the tin reagent having the chelating properties ['R_3SnCu' or '$R_3Sn(Et_2)ZnLi$'] provided with high stereoselectivity the stannyl derivative **33** with the (*R*)-configuration at the newly created stereogenic center. It is interesting to note, that stannyllithium, under the same conditions, afforded the opposite (*S*)-isomer **32** (Fig. 9).

Although the reaction studied by us (S_N2' displacement) is different, we may assume similar stereoselectivity as reported by Krief. Allylic derivatives: **8**, **21**, and **25** having the opposite (*R*)-configuration at the C-α atom afforded, therefore, almost exclusively the secondary stannyl isomers with the (*S*)-configuration at the newly created stereogenic center.



(*Z*)-**31** +	'R_3SnCu'	10	***90***
(*E*)-**31** +	'R_3SnCu'	43	***57***
(*Z*)-**31** +	'$R_3Sn(Et_2)ZnLi$'	0	***100***
(*E*)-**31** +	'$R_3Sn(Et_2)ZnLi$'	10	***90***
(*Z*)-**31** +	R_3SnLi	74	26
(*E*)-**31** +	R_3SnLi	100	0

Figure 9. The 1,4-addition of tin species to unsaturated sugar esters.

4. Summary

Reaction of tributyltin cuprate with primary allylic mesylates, derivatives of the D-sugars proceeds preferentially in an S_N2' mode to yield the secondary sugar allyltin derivatives as single stereoisomers with the (*S*)-configuration at the newly created stereogenic center. Thermal decomposition of these compounds affords the dienoaldehydes [CH_2=CH-CH=CH-[$(CHOR)_3$]-CHO] with the *cis*-geometry across the internal double bond. This thermal method is complementary to the controlled decomposition induced with Lewis acids, which provides the *trans*-dienoaldehydes.

5. Experimental

5.1. General

Optical rotations were measured with a JASCO DIP 360 automatic polarimeter at 20±2°C. NMR spectra were recorded with Varian Gemini AC-200 (200 MHz), Varian Mercury (400 MHz), or Bruker AM-500 (500 MHz) spectrometers in $CDCl_3$ solutions with Me_4Si as an internal standard. ^1H and ^{13}C signals of aromatic groups occurred at the expected chemical shifts were omitted in the description of spectra. ^{13}C NMR spectra were recorded in the DEPT 135 mode. The proton and carbon resonances in the spectra of most compounds were assigned by the COSY and HETCOR correlations. Mass spectra were recorded on an AMD-604 mass spectrometer. HPLC was carried out on a Shimadzu instrument: central unit C-R4A, pump unit LC-8A, UV detector SPD-6A on a column Machery–Nagel Nucleosil 100-7. TLC was performed on Silica Gel HF-254 ready plates and column chromatography on Silica Gel 230–400 or 70–230 mesh (E. Merck). Organic solutions were dried over anhydrous magnesium or sodium sulfate.

5.2. Starting materials

Sugar allylic derivatives: **8d**, (*E*)-**25**,[17] and (*Z*)-**25** were prepared from the corresponding allylic alcohols: methyl 2,3,4-tri-*O*-benzyl-6,7-dideoxy-oct-6(*E*)-eno-α-D-*manno*-1,5-pyranoside[5,15] **8**, methyl 2,3-di-*O*-benzyl-5,6-di-de-oxy-hept-5(*E*)-eno-β-D-ribo-furanoside[16] or its 5(*Z*) isomer by standard mesylation with MsCl in pyridine at 0°C. Halogeno derivatives **8a**,**b** were prepared by Appel reaction performed on **8** (CCl_4/Ph_3P or CBr_4/Ph_3P). Iodide **8c** was prepared from chloride **8b** by the S_N2 reaction with sodium iodide in refluxing acetone.

5.2.1. Methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-chloro-oct-6-(*E*)-eno-α-D-manno-1,5-pyranoside 8a. $[\alpha]_D$ +41.3 (*c* 1.0, $CHCl_3$). ^1H NMR (200 MHz) δ: 6.01 (ddd, $J_{6,7}$ 15.4, $J_{7,8a}$ 6.2, $J_{7,8b}$ 5.6 Hz, H-7), 5.88 (dd, $J_{5,6}$ 5.4 Hz, H-6), 4.70 (m, 3×CH_2Ph), 4.62 (d, $J_{1,2}$ 1.0 Hz, H-1), 4.04 (dd, $J_{4,5}$ 9.0 Hz, H-5), 4.01 (d, H-8a, H-8b), 3.87 (dd, $J_{2,3}$ 3.0, $J_{3,4}$ 9.4 Hz, H-3), 3.77 (dd, H-2), 3.69 (d, H-4), 3.27 (s, OCH_3). ^{13}C NMR (200 MHz) δ: 138.4, 138.2, 138.1 (3×C_{quat} benzyl), 131.8 (C-7), 128.7 (C-6), 99.1 (C-1), 79.7 and 78.3 (C-3,4), 74.6, 71.3 (C-2, 5), 75.0, 72.7, 72.2 (3×CH$_2$Ph), 54.7 (OCH$_3$), 44.3 (C-8). Anal. calcd for $C_{30}H_{33}O_5Cl$: C, 70.78; H, 6.53; Cl, 6.96. Found: C, 70.64; H, 6.44; Cl, 7.00.

5.2.2. Methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-bromo-oct-6-(*E*)-eno-α-D-manno-1,5-pyranoside 8b. $[\alpha]_D$ +27.4 (*c* 1.0, $CHCl_3$).^1H NMR (200 MHz) δ: 6.07 (ddd, $J_{6,7}$ 15.2, $J_{7,8a}$ 7.6 Hz, H-7), 5.87 (dd, $J_{5,6}$ 6.2 Hz, H-6), 4.75 (m, 3×CH_2Ph), 4.63 (d, $J_{1,2}$ 0.8 Hz, H-1), 4.03 (dd, $J_{4,5}$ 9.4 Hz, H-5), 3.91 (d, H-8a, H-8b), 3.86 (dd, $J_{2,3}$ 3.2, $J_{3,4}$ 9.3 Hz, H-3), 3.77 (dd, H-2), 3.69 (d, H-4), 3.29 (s, OCH_3). ^{13}C NMR (200 MHz) δ: 138.5, 138.3, 138.2 (3×C_{quat} benzyl), 132.5 (C-7), 129.2 (C-6), 99.2 (C-1), 79.8 and 78.4 (C-3,4), 74.7, 71.4 (C-2,5), 75.1, 72.8, 72.4 (3×CH$_2$Ph), 54.8 (OCH$_3$), 32.4 (C-8). HRMS m/z: 575.13924 [$C_{30}H_{33}O_5{}^{79}BrNa$ (M+Na$^+$) requires 575.14091]. Anal. calcd for $C_{30}H_{33}O_5Br$: C, 65.10; H, 6.01; Br, 14.43. Found: C, 64.92; H, 5.97; Br, 14.66.

5.2.3. Methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-iodo-oct-6-(*E*)-eno-α-D-manno-1,5-pyranoside 8c. $[\alpha]_D$ +3.2 (*c* 0.6, $CHCl_3$). ^1H NMR (200 MHz) δ: 6.09 (ddd, $J_{6,7}$ 15.2, $J_{7,8}$ 7.4 Hz, H-7), 5.87 (dd, $J_{5,6}$ 6.8 Hz, H-6), 4.70 (m, 3×CH_2Ph), 4.62 (s, H-1), 4.00 (dd, $J_{4,5}$ 9.4 Hz, H-5), 3.85 (m, H-8a, H-8b, H-3), 3.75 (dd, $J_{1,2}$ 2.0 Hz, H-2), 3.68 (d, H-4), 3.27 (s, OCH_3). ^{13}C NMR (200 MHz) δ: 138.4, 138.3, 138.1 (3×C_{quat} benzyl), 131.1 (C-7), 130.8 (C-6), 99.1 (C-1), 79.6 and 78.4 (C-3,4), 74.6, 71.4 (C-2,5), 74.9, 72.7, 72.3 (3×CH$_2$Ph), 54.72 (OCH$_3$), 4.7 (C-8). Anal. calcd for $C_{30}H_{33}O_5I$: C, 60.00; H, 5.53; I, 21.13. Found: C, 60.01; H, 5.67; I, 20.85.

5.2.4. Methyl 2,3,4-tri-*O*-benzyl-6,7-dideoxy-8-*O*-mesyl-oct-6-(*E*)-eno-α-D-manno-1,5-pyranoside 8d. $[\alpha]_D$ +45.1 (*c* 1.2, $CHCl_3$). ^1H NMR (200 MHz) δ: 6.00 (m, H-6, H-7), 4.74 (m, 3×CH_2Ph, H-8a, H-8b), 4.63 (s, H-1), 4.05 (dd, $J_{4,5}$ 9.8, $J_{5,6}$ 3.2 Hz, H-5), 3.88 (dd, $J_{2,3}$ 3.0, $J_{3,4}$ 9.4 Hz, H-3), 3.79 (dd, $J_{1,2}$ 2.0 Hz, H-2), 3.68 (d, H-4), 3.29 (s, OCH_3), 2.91 (s, SO_2CH_3). ^{13}C NMR (200 MHz) δ: 138.3, 138.2, 138.1 (3×C_{quat} benzyl), 134.3 (C-7), 124.6 (C-6), 99.2 (C-1), 79.8 and 78.20 (C-3,4), 74.5, 71.0 (C-2,5), 75.0, 72.8, 72.2 (3×CH$_2$Ph), 69.5 (C-8), 54.7 (OCH$_3$), 37. 9 (SO_2CH_3). Anal. calcd for $C_{31}H_{36}O_8S$: C, 65.47; H, 6.38; S, 5.94. Found: C, 65.71; H, 6.56; S, 5.84.

5.2.5. Methyl 2,3-di-*O*-benzyl-5,6-dideoxy-7-*O*-mesyl-hept-5-(*E*)-eno-β-D-ribo-furanoside (*E*)-25. $[\alpha]_D$ +22.0 (*c* 1.2, $CHCl_3$). ^1H NMR (200 MHz) δ: 5.90 (m, H-5, H-6), 4.90 (s, H-1), 4.57 (m, CH_2Ph, H-4), 4.64 (d, $J_{6,7a}=J_{6,7b}$ 3.0 Hz, H-7a, H-7b), 4.58 and 4.44 (d, $J_{A,B}$ 12.0 Hz, CH_2Ph), 3.90 (dd, $J_{2,3}$ 4.4, $J_{3,4}$ 7.2 Hz, H-3), 3.84 (dd, $J_{1,2}$ 0.8 Hz, H-2), 3.34 (s, OCH_3), 2.95 (s, SO_2CH_3). ^{13}C NMR (200 MHz) δ: 137.5, 137.4 (2×C_{quat} benzyl), 136.4 and 124.4 (C-5,6), 106.3 (C-1), 81.7, 80.3, 79.5 (C-2,3,4), 72.5, 72.3 (2×CH_2Ph), 69.3 (C-7), 55.2 (OCH_3), 38.1 (SO_2CH_3). HRMS *m*/*z*: 471.14365 [$C_{23}H_{28}O_7SNa$ ($M+Na^+$) requires 471.14535].

5.2.6. Methyl 2,3-di-*O*-benzyl-5,6-dideoxy-7-*O*-mesyl-hept-5-(*Z*)-eno-β-D-ribo-furanoside (*Z*)-25. $[\alpha]_D$ −17.4 (*c* 1.0, $CHCl_3$). ^1H NMR (200 MHz) δ: 5.73 (m, H-5,H-6), 4.89 (s, H-1), 4.86 (m, CH_2Ph, H-4), 4.64 (d, $J_{6,7a}=J_{6,7b}$ 4.4 Hz, H-7a, H-7b), 4.54 and 4.41 (d, $J_{A,B}$ 12.0 Hz, CH_2Ph), 3.90 (dd, $J_{3,4}$ 7.8 Hz, H-3), 3.83 (d, $J_{2,3}$ 4.4 Hz, H-2), 3.33 (s, OCH_3), 2.89 (s, SO_2CH_3). ^{13}C NMR (200 MHz) δ: 2×137.4 (2×C_{quat} benzyl), 135. 5, 125.3 (C-5,6), 106.4 (C-1), 82.3, 79.1, 76.5 (C-2,3,4), 72.6, 72.4 (2×CH_2Ph), 65.6 (C-7), 55.1 (OCH_3), 37.6 (SO_2CH_3). HRMS *m*/*z*: 471.14657 [$C_{23}H_{28}O_7SNa$ ($M+Na^+$) requires 471.14535].

5.3. General method of the reaction of tributyltin cuprate with sugar electrophiles

5.3.1. Preparation of tributyltin cuprate. ***Method a***. To a cooled (to −78°C) and stirred suspension of CuCN (270 mg, 3 mmol) in dry THF (10 mL) a solution of butyllithium in hexane (6 mmol) was added and the mixture was stirred for 10 min. To a slightly yellow solution of resulting organocuprate, tri-*n*-butyltin hydride (neat, 6 mmol) was added by a syringe at −78°C. After evolution of gas ceased the yellow mixture was stirred for 30 min at −78°C to yield a solution of crude tri-*n*-butyltin cuprate.

Method b. This reaction was performed analogously as in ***method a***, except that the 'Bu$_3$SnCu' was generated for 90 min at −82°C (methanol/solid CO_2).

5.3.2. General procedure for reaction of 'Bu$_3$SnCu' with sugar electrophiles. A solution of appropriate sugar electrophile (1 mmol in 5 mL of dry THF) was added by a syringe to a solution of above prepared tributyltin cuprate in THF and the mixture was stirred at the required temperature until TLC showed disappearance of the starting material (hexane–ethyl acetate, 10:1). The mixture was diluted with ether (15 mL), aqueous saturated ammonium chloride (5 mL) was added and the mixture was stirred for 30 min at rt. Organic layer was separated, washed with water, dried and concentrated and the crude product was isolated by column chromatography (hexane–diethyl ether, 95:5 and then hexane–ethyl acetate, 15:1) and further purified by HPLC (hexane–ethyl acetate, 20:1).

5.4. Reaction of allyl pyranosides with 'Bu$_3$SnCu'

Reaction of the D-*gluco*-configurated sugar mesylate **21** with 'Bu$_3$SnCu' afforded known allyltins: **22** (primary) and **23**[6] (secondary, one isomer) in the ratio 1:1 (***method a***) or 1:2 (***method b***).

The D-*manno*-configurated derivatives **8a–d** was reacted with 'Bu$_3$SnCu' according either to ***method a*** or ***method b*** to afford the corresponding allyltin derivatives **9** and **10** together with butylated products **11** and **12**. The results are shown in Table 1.

5.4.1. Methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-6(*S*)-(tri-*n*-butylstannyl)-oct-7-eno-α-D-manno-1,5-pyranoside (*S*)-9. ^1H NMR (500 MHz) δ: 6.21 (m, $J_{6,7}=J_{7,8a}$ 10.6, $J_{7,8b}$ 17.3 Hz, H-7), 4.84 (m, 2×CH_2Ph, H-8a, H-8b), 4.65 (m, 2×CH_2Ph), 4.64 (d, $J_{1,2}$ 1.7 Hz, H-1), 3.97 (dd, $J_{3,4}$ 9.4, $J_{4,5}$ 9.3 Hz, H-4), 3.84 (dd, $J_{2,3}$ 2.9 Hz, H-3), 3.74 (m, H-2, H-5), 3.31 (s, OCH_3), 2.82 (dd, $J_{5,6}$ 2.3 Hz, H-6), 1.49 [m, Sn($CH_2CH_2CH_2CH_3$)$_3$], 1.30 [m, Sn($CH_2CH_2CH_2CH_3$)$_3$], 0.90 [t, *J* 9.0 Hz, [m, Sn($CH_2CH_2CH_2CH_3$)$_3$], 0.89 [t, *J* 7.3 Hz, Sn($CH_2CH_2CH_2CH_3$)$_3$]. ^{13}C NMR (500 MHz) δ: 139.2, 138.8, 138.7 (3×C_{quat} benzyl), 138.5 (C-7), 110.6 (C-8), 99.5 (C-1), 80.1 (C-3), 77.4 (C-4), 75.4 and 74.0 (C-2,5), 74.8, 72.5, 72.2 (3×CH_2Ph), 55.7 (OCH_3), 35.0, (C-6), 29.2, and 27.5 ($SnCH_2CH_2CH_2CH_3$), 13.7 ($SnCH_2CH_2CH_2CH_3$), 9.4 ($SnCH_2CH_2CH_2CH_3$). HRMS *m*/*z*: 707.27551 [$C_{38}H_{51}O_5{}^{120}Sn$ ($M+H^+$) requires 707.27585].

5.4.2. Methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-6(*R*)-(tri-*n*-butylstannyl)-oct-6-eno-α-D-manno-1,5-pyranoside (*R*)-9. This compound could not be isolated in a pure form and its presence was detected only from the NMR spectra of highly enriched mixture of (*R*)-**9**/(*S*)-**9**.

^1H NMR (500 MHz) δ: 6.02 (ddd, $J_{7,8a}$ 10.3, $J_{7,8b}$ 17.0 Hz, H-7), 4.73 (m, 3×CH_2Ph), 4.77 (d, H-8b), 4.65 (d, H-8a), 4.60 (s, H-1), 3.87 (dd, $J_{3,4}$ 9.4, $J_{2,3}$ 3.7 Hz, H-3), 3.83 (dd, $J_{4,5}$ 9.0 Hz, H-5), 3.74 (dd, $J_{1,2}$ 2.0 Hz, H-2), 3.55 (dd, H-4), 3.32 (s, OCH_3), 2.63 (dd, $J_{5,6}$ 4.6 Hz, H-6), 1.47 [m, Sn($CH_2CH_2CH_2CH_3$)$_3$], 1.39 [m, Sn($CH_2CH_2CH_2CH_3$)$_3$, 0.89 [m, Sn($CH_2CH_2CH_2CH_3$)$_3$]. ^{13}C NMR (500 MHz) δ: 140.8 (C-7), 138.8, 138.7, 138.5 (3×C_{quat} benzyl), 107.6 (C-8), 99.1 (C-1), 80.4 and 79.6 (C-3,4), 75.3 and 74.7 (C-2,5), 74.6, 72.7, 72.1 (3×CH_2Ph), 55.1 (OCH_3), 38.7 (C-6), 29.3, 27.46 [Sn($CH_2CH_2CH_2CH_3$)$_3$], 13.8 [Sn($CH_2CH_2CH_2CH_3$)$_3$], 10.1 [Sn($CH_2CH_2CH_2CH_3$)$_3$].

5.4.3. Methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-(tri-*n*-butylstannyl)-oct-6(*E*)-eno-α-D-manno-1,5-pyranoside 10. This isomer was identical in all respects with the compound prepared previously.[5]

5.4.4. Methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-6-butyl-oct-7-eno-α-D-manno-1,5-pyranoside 11. $[\alpha]_D$ −10.0 (*c* 0.7, $CHCl_3$). ^1H NMR (400 MHz) δ: 5.91 (ddd, $J_{7,8a}$ 10.2, $J_{7,8b}$ 17.1 Hz, H-7), 5.15 (dd, $J_{6,8a}$ 1.9 Hz, H-8a), 5.01 (dd, $J_{6,8b}$ 2.1 Hz, H-8b), 4.94 (d, 1H, $J_{A,B}$

10.9 Hz, CH_2Ph), 4.65 (m, 5H, 3×CH_2C$_6$H$_5$), 4.59 (d, $J_{1,2}$ 0.8 Hz, H-1),, 3.85 (dd, $J_{3,4}$ 9.3 Hz, H-3), 3.83 (dd, $J_{4,5}$ 9.0 Hz, H-4) 3.75 (dd, $J_{2,3}$ 2.3 Hz, H-2), 3.58 (dd, $J_{5,6}$ 5.2, $J_{5,7}$ 1.9 Hz, H-5), 3.30 (s, OCH_3), 2.54 (ddd, $J_{6,7}$ 9.2 Hz, H-6), 1.30 (m, CH_2CH_2CH_2CH$_3$), 0.88 (t, J 6.9 Hz, CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (400 MHz) δ: 138.5 (C-7), 2×138.9 and 138.5 (3×C$_{quat}$ benzyl), 117.1 (C-8), 98.8 (C-1), 80.6, 76.1, 74.7, 74.0, (C-2,3,4,5), 74.7, 72.3, 71.9 (3×CH$_2$Ph), 54.6 (OCH$_3$), 44.2 (C-6), 31.8, 29.8, 22.7 (CH$_2$$CH_2$$CH_2CH_3$), 14.2, (CH$_2CH_2CH_2$$CH_3$). HRMS m/z: 553.2919 [C$_{34}H_{42}O_5$Na (M+Na$^+$) requires 553.2924].

5.4.5. Methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-butyl-oct-6-(*E*)-eno-α-D-manno-1,5-pyranoside 12. ^{1}H NMR (200 MHz) δ: 5.88 (ddd, $J_{7,8a}$ 6.6, $J_{7,6}$ 15.4 Hz, H-7), 5.58 (dd, $J_{5,6}$ 7.6 Hz, H-6), 4.70 (m, 3×CH_2Ph), 4.63 (s, H-1), 3.96 (dd, $J_{4,5}$ 9.0 Hz, H-5), 3.86 (dd, $J_{3,4}$ 9.3, $J_{2,3}$ 3.1 Hz, H-3), 3.77 (dd, $J_{1,2}$ 2.0 Hz, H-2), 3.71 (dd, H-4), 3.29 (s, OCH_3), 2.08 (m, H-8a, H-8b), 1.25 (m, CH_2CH_2CH_2CH$_3$), 0.87 (t, J 6.9 Hz, CH$_2$CH$_2$CH$_2$-CH_3). ^{13}C NMR (200 MHz) δ: 138.6, 138.5, 138.3 (3×C$_{quat}$ benzyl), 135.9 and 127.2 (C-6,7), 99.0 (C-1), 79.7 and 78.9 (C-3,4), 74.9, 73.1 (C-2,5), 75.0, 72.7, 72.3 (3×CH$_2$Ph), 54.7 (OCH$_3$), 32.4 (C-8), 31.5, 28.6, 22.5 (CH$_2$$CH_2$$CH_2CH_3$), 14.0 (CH$_2CH_2CH_2$$CH_3$). HRMS m/z: 553.2930 [C$_{34}H_{42}O_5$Na (M+Na$^+$) requires 553.2924].

5.5. Reaction of allyl furanosides with 'Bu$_3$SnCu'

This reaction was performed under conditions described in ***method b***.

Reaction of mesylate (*E*)-25 with 'Bu$_3$SnCu' provided allyltins (*E*)-**26** (primary, 47%), and **27** (secondary, 16%, single isomers) together with minute amounts of butylated product **29** (5%, single isomer).

Reaction of mesylate (*Z*)-**25** with 'Bu$_3$SnCu' provided allyltins (*Z*)-**26** (primary, 6%), and **27** (secondary, 19%, contaminated with ca. 2% of the opposite isomer) together with butylated products (*Z*)-**28** (13%) and **29** (45%, ca. 1:1 mixture of stereoisomers).

5.5.1. Methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-7-(tri-*n*-butyl)stannyl-hept-5-(*E*)-eno-β-D-ribo-furanoside (*E*)-26[16]. ^{1}H NMR (400 MHz) δ: 5.92 (ddd, $J_{5,6}$ 15.0 Hz, H-6), 5.21 (dd, $J_{4,5}$ 8.4 Hz, H-5), 4.86 (s, H-1), 4.65 and 4.56 (d, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.59 and 4.51 (d, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.51 (dd, $J_{3,4}$ 7.4 Hz, H-4), 3.84 (dd, H-3), 3.81 (dd, $J_{1,2}$ 0.6, $J_{2,3}$ 4.5 Hz, H-2), 3.34 (s, OCH_3), 1.77 (dd, $J_{5,7a}$ 1.0, $J_{6,7a}$ 8.8 Hz, H-7a), 1.76 (dd, $J_{5,7b}$ 0.9, $J_{6,7b}$ 8.4 Hz, H-7b), 1.46 and 1.28 (m, SnCH$_2$CH_2CH_2CH$_3$), 0.87 (m, SnCH_2CH$_2$CH$_2$CH_3). ^{13}C NMR (400 MHz) δ: 138.0, 137.9 (2×C$_{quat}$ benzyl), 135.2, 124.5 (C-5,6), 105.6 (C-1), 82.8, 82.4, 80.1 (C-2,3,4), 72.5, 72.2 (2×CH$_2$Ph), 54.9 (OCH$_3$), 29.0, 27.3 (SnCH$_2$$CH_2$$CH_2CH_3$), 14.50 (C-7), 13.7 (SnCH$_2$-CH$_2$CH$_2$$CH_3$), 9.1 (Sn$CH_2CH_2CH_2CH_3$).

5.5.2. Methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-7-(tri-*n*-butyl)stannyl-hept-5-(*Z*)-eno-β-D-ribo-furanoside (*Z*)-26[16]. ^{1}H NMR (400 MHz) δ: 5.80 (ddd, $J_{5,6}$ 9.1 Hz, H-6), 5.07 (dd, $J_{4,5}$ 9.2 Hz, H-5), 4.92 (dd, $J_{3,4}$ 6.8 Hz, H-4), 4.88 (d, $J_{1,2}$ 0.7 Hz, H-1), 4.69 and 4.64 (d, $J_{A,B}$ 12.2 Hz, CH_2Ph), 4.54 and 4.53 (d, $J_{A,B}$ 12.0 Hz, CH_2Ph), 3.88 (dd, $J_{2,3}$ 4.7 Hz, H-3), 3.82 (dd, H-2), 3.32 (s, OCH_3), 1.93 (ddd, $J_{5,7a}$ 1.1, $J_{6,7a}$ 10.2, $J_{7a,7b}$ 11.3 Hz, H-7a), 1.80 (ddd, $J_{5,7b}$ 0.9, $J_{6,7b}$ 8.9 Hz, H-7b), 1.47 and 1.26 (m, SnCH$_2$CH_2CH_2CH$_3$), 0.89 (m, SnCH_2CH$_2$-CH$_2$CH_3). ^{13}C NMR (400 MHz) δ: 138.1, 138.0 (2×C$_{quat}$ benzyl), 134.2, 123.7 (C-5,6), 106.0 (C-1), 82.9, 80.5, 76.7 (C-2,3,4), 2×72.3 (2×CH$_2$Ph), 54.9 (OCH$_3$), 29.1, 27.3 (SnCH$_2$$CH_2$$CH_2CH_3$), 13.7 (SnCH$_2CH_2$-CH$_2$$CH_3$), 11.20 (C-7), 9.3 (Sn$CH_2CH_2CH_2CH_3$).

5.5.3. Methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-(5*S*)-(tri-*n*-butyl)stannyl-hept-6-eno-β-D-ribo-furanoside 27. ^{1}H NMR (500 MHz) δ: 5.88 (ddd, $J_{6,7a}$ 17.2, $J_{6,7b}$ 10.7 Hz, H-6), 4.81 (s, H-1), 4.79 (dd, $J_{5,7a}$ 1.8 Hz, H-7a), 4.75 (dd, $J_{5,7b}$ = 2.0 Hz, H-7b), 4.67 and 4.60 (d, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.53 and 4.44 (d, $J_{A,B}$ 11.8 Hz, CH_2Ph), 4.35 (dd, $J_{3,4}$ 8.0, $J_{4,5}$ 4.1 Hz, H-4), 3.89 (dd, $J_{2,3}$ 4.7 Hz, H-3), 3.78 (d, H-2), 3.35 (s, OCH_3), 2.43 (dd, $J_{5,6}$ 11.0 Hz, H-5), 1.47 and 1.29 (SnCH$_2$CH_2CH_2CH$_3$), 0.88 (SnCH_2CH$_2$CH$_2$CH_3). ^{13}C NMR (500 MHz) δ: 138.07 (C-6), 137.9, 137.8 (2×C$_{quat}$ benzyl), 110.4 (C-7), 105.2 (C-1), 82.8 (C-4), 80.3 (C-2), 79.0 (C-3), 72.2, 72.1 (2×CH$_2$Ph), 55.0 (OCH$_3$), 35.7 (C-5), 29.1, 27.4 (SnCH$_2$$CH_2$$CH_2CH_3$), 13.7 (SnCH$_2CH_2CH_2$$CH_3$), 9.3 (Sn$CH_2CH_2CH_2CH_3$). HRMS m/z: 667.2780 [C$_{34}H_{52}O_4$SnNa (M+Na$^+$) requires 667.2799].

In the NMR spectra of **27** obtained from (*Z*)-**25** additional resonances at δ 3.83 and 2.37 (^{1}H) and 109.9, 105.8, and 55.7 (^{13}C) ppm were observed. Although it was not possible to establish precisely the structure of the compound present in ca. 10% in the mixture, it was assumed to be the alternative 5*R* isomer on the basis of the decomposition experiment (see Section 5.6).

5.5.4. Methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-7-*C*-(butyl)-hept-5-(*Z*)-eno-β-D-ribo-furanoside (*Z*)-28. $[\alpha]_D$ –2.1 (*c* 1.0, CHCl$_3$). ^{1}H NMR (400 MHz) δ: 5.71 (ddd, $J_{6,7a}$ 6.9, $J_{6,7b}$ 7.2 Hz, H-6), 5.40 (ddd, $J_{5,7}$ 1.6 Hz, $J_{5,6}$ 11.0 Hz, H-5), 4.98 (ddd, $J_{4,6}$ 0.9, $J_{4,5}$ 8.4 Hz, H-4), 4.88 (s, H-1), 4.70 and 4.65 (d, $J_{A,B}$ 12.3 Hz, CH_2Ph), 4.55 and 4.50 (d, $J_{A,B}$ 12.1 Hz, CH_2Ph), 3.90 (dd, $J_{3,4}$ 7.3 Hz, H-3), 3.84 (d, $J_{2,3}$ 4.6 Hz, H-2), 3.32 (s, OCH_3), 1.75 (d, H-7b), 1.74 (d, H-7a), 1.64, 1.36 and 1.31 (m, CH_2CH_2CH_2CH$_3$), 0.92 (t, J 7.3 Hz, CH$_2$CH$_2$CH$_2$-CH_3). ^{13}C NMR (400 MHz) δ: 137.9, 137.8 (2×C$_{quat}$ benzyl), 130.4, 128.9 (C-5,6), 106.1 (C-1), 82.6, 80.1, 76.5 (C-2,3,4), 72.4, 72.3 (2×CH$_2$Ph), 54.9 (OCH$_3$), 27.8, 26.8, 17.5 (CH$_2$$CH_2$$CH_2CH_3$), 13.6 (CH$_2CH_2$-CH$_2$$CH_3$), 13.3 (C-7). HRMS m/z: 433.2389 [C$_{26}$H$_{34}$O$_4$Na (M+Na$^+$) requires 433.2349].

5.5.5. Methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-5-*C*-(butyl)-hept-6-eno-β-D-ribo-furanoside 29. One isomer obtained in reaction of (*E*)-**25**: $[\alpha]_D$ +19.7 (*c* 0.6, CHCl$_3$). ^{1}H NMR (200 MHz) δ: 5.59 (ddd, $J_{6,7b}$ 17.1 Hz, $J_{6,7a}$ 10.0 Hz, H-6), 5.40 (dd, $J_{5,7a}$ 1.8 Hz, H-7a), 4.88 (dd, $J_{5,7b}$ 2.2 Hz, H-7b), 4.84 (s, H-1), 4.68 and

4.56 (d, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.54 and 4.38 (d, $J_{A,B}$ 11.9 Hz, CH_2Ph), 4.12 (dd, $J_{3,4}$ 8.1, $J_{4,5}$ 4.3 Hz, H-4), 3.91(dd, $J_{2,3}$ 4.6 Hz, H-3), 3.78 (d, H-2), 3.31 (s, OCH_3), 2.12 (m, $J_{5,6}$ 9.2 Hz, H-5), 1.27 (m, CH_2CH_2CH_2CH$_3$), 0.87 (t, J 6.6 Hz. CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (200 MHz) δ: 138.6 (C-6), 2×137.8 (2×C_{quat} benzyl), 116.8 (C-7), 105.6 (C-1), 83.1, 79.4, 79.1, (C-2,3,4), 72.3, 72.2 (2×CH$_2$Ph), 54.9 (OCH$_3$), 47.4 (C-5), 31.3, 29.4, 22.6 (CH$_2C$H$_2C$H$_2$CH$_3$), 14.0 (CH$_2$CH$_2$CH$_2C$H$_3$). HRMS m/z: 433.2368 [$C_{26}H_{34}O_4Na$ (M+Na$^+$) requires 433.2349].

In a mixture of isomers of **29** obtained from (*Z*)-**25** besides the signals of the isomer listed above, additional signals in the ^{13}C NMR spectrum that could be connected with the epimer at the C-5 were seen: ^{13}C NMR (200 MHz) δ: 137.8 (C-6), 116.0 (C-7), 106.0 (C-1), 83.7, 80.5, 79.81, (C-2,3,4), 49.9 (C-5), 30.6, 29.0, 26.8 (CH$_2C$H$_2C$H$_2$CH$_3$), 13.6 (CH$_2$CH$_2$CH$_2C$H$_3$).

5.6. Thermal degradation of secondary sugar allyltins

Degradation of the D-*manno*- and D-*gluco*-configurated derivatives [(*S*)-**9** and **23**] performed at 140°C as described in Ref. 14 afforded the *cis*-dienoaldehydes **15** and **24**, respectively.[14]

5.6.1. Methyl (4*S*,5*R*)-di-benzyloxy-(2*E*,6*Z*),8-trienononate 31. Secondary sugar allyltin **27** (obtained from mesylate (*E*)-**25**; 130 mg, 0.2 mmol) was dissolved in dry xylene (4 mL) containing Ph$_3$P=CH-CO$_2$Me (130 mg, 0.4 mmol) and boiled at 120°C until TLC (hexane–ethyl acetate, 10:1) indicated disappearance of the starting material and formation of a new, more polar product that was visible under the UV light (8 h). The mixture was cooled to rt, concentrated and the residue was subjected to column chromatography (hexane–diethyl ether, 95:5 than hexane–ethyl acetate, 15:1) to yield pure triene **31** (54 mg, 71%) as single isomer. $[\alpha]_D$ −29.0 (*c* 1.1, CHCl$_3$). ^{1}H NMR (500 MHz) δ: 6.97 (dd, $J_{3,4}$ 6.1, $J_{2,3}$ 15.8 Hz, H-3), 6.44 (ddd, $J_{7,8}=J_{8,9a}$ 11.0, $J_{8,9b}$ 16.7 Hz, H-8), 6.29 (dd, $J_{6,7}$ 11.2 Hz, H-7), 6.07 (dd, $J_{2,4}$ 1.3 Hz, H-2), 5.42 (dd, H-6), 5.27 (dd, $J_{9,9b}$ 0.8 Hz, H-9b), 5.16 (d, H-9a), 4.61 (d, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.46 and 4.39 (d, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.37 (ddd, $J_{5,6}$ 9.3, $J_{5,7}$ 0.8 Hz, H-5), 4.03 (ddd, $J_{4,5}$ 5.2 Hz, H-4), 3.74 [s, C(O)OCH_3]. ^{13}C NMR (500 MHz) δ: 166.4 (C-1), 145.3 (C-3), 138.0, 137.8 (2×C_{quat} benzyl), 134.2 (C-7)9, 131.7 (C-8), 123.0 (C-2), 119.9 (C-9), 80.2 (C-4), 76.1 (C-5), 71.6, 70.3 (2×CH$_2$Ph), 51.6 [C(O)OCH$_3$]. HRMS m/z: 401.1738 [$C_{24}H_{36}O_4Na$ (M+Na$^+$) requires 401.1723].

Compound **27** obtained from (*Z*)-**25** (contaminated with ca. 10% of the opposite stereoisomer) was decomposed analogously to afford **31** containing ca. 10% of the 6(*E*)-isomer of **31**–**31′**. This derivative was identified by comparison with the authentic sample prepared independently (see below).

5.6.2. Methyl (4*S*,5*R*)-dibenzyloxy-(2*E*,6*E*),8-trienononate 31′. Primary allyltin derivative (*E*)-**26** was decomposed to known *trans*-dienoaldehyde **30′** by treatment with zinc chloride in CH$_2$Cl$_2$.[16] This aldehyde (65 mg, 0.2 mmol) was dissolved in benzene (5 mL) to which Ph$_3$P=CH-CO$_2$Me was added and the mixture was kept at rt for 3 h. Solvent was removed in vacuum and the residue was purified by column chromatography (hexane–ethyl acetate, 15:1) to afford pure **31′** (80%, 60 mg, 0.16 mmol). ^{1}H NMR (500 MHz) δ: 6.96 (dd, $J_{3,4}$ 6.0, $J_{2,3}$ 15.8 Hz, H-3), 6.37 (ddd, $J_{8,9b}$ 17.0 Hz, H-8), 6.26 (dd, $J_{6,7}$ 15.3, $J_{7,8}$ 10.6 Hz, H-7), 6.07 (d, H-3), 5.65 (dd, $J_{5,6}$ 7.8 Hz, H-6), 5.25 (d, H-9b), 5.15 (d, $J_{8,9a}$ 9.9 Hz, H-9a), 2×4.60 (d, $J_{A,B}$ 12.1 Hz, CH_2Ph), 4.46 and 4.39 (d, $J_{A,B}$ 12.0 Hz, CH_2Ph), 4.03 (dd, H-4), 3.92 (dd, $J_{4,5}$ 5.6 Hz, H-5), 3.76 [s, C(O)OCH_3]. ^{13}C NMR (500 MHz) δ: 166.4 (C-1), 145.5 (C-3), 138.1, 137.8 (2×C_{quat} benzyl), 136.1 (C-7), 135.2 (C-8), 130.3 (C-6), 123.0 (C-2), 118.3 (C-9), 81.2 and 80.3 (C-4,5), 71.7, 70.6 (2×CH$_2$Ph), 51.6 [C(O)OCH$_3$].

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