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Mechanism of the fragmentation of secondary sugar allyltin derivatives

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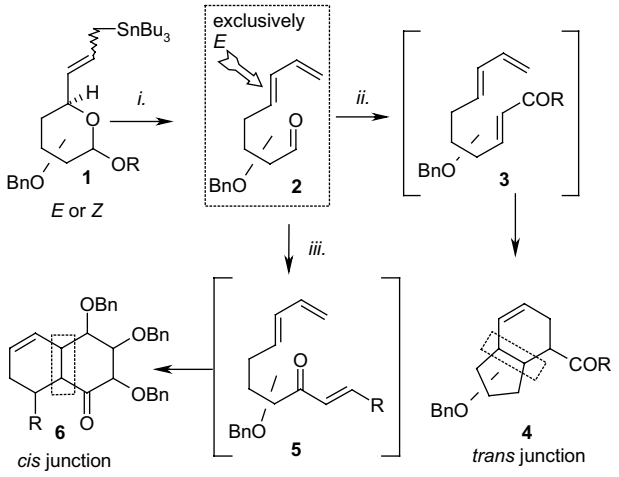
Dedicated to Professor Mieczysław Mąkosza on the occasion of his 70th birthday

Abstract—Secondary sugar allyltin derivatives (obtained in an S_N2' reaction of the corresponding primary allylic mesylates with 'Bu_3SnCu') decompose at high temperatures with elimination of the stannyl moiety and opening of the sugar ring. The product—a dienoaldehyde with a *cis*-geometry across the internal double bond—is formed via the *anti*-(*E*2)-elimination process as proven by the ^{117}Sn NMR spectroscopy.

1. Introduction

Over the past few years, we have elaborated a convenient methodology of the synthesis of enantiomerically pure, highly oxygenated bicyclic derivatives, such as **4** or **6**, from sugar allyltins.[1] The key compound, dienoaldehyde **2** with an *E*-configuration across the internal double bond, is readily prepared by a Lewis acid induced, decomposition of the primary sugar allyltins **1**, regardless of their geometry (*E* or *Z*).[2] Further transformations of **2** either into trienes **3** or **5** followed by the intramolecular Diels-Alder reaction provided the *trans*-bicyclo [4.3.0]nonene **4**[3] or *cis*-bicyclo[4.4.0]decene **6**[4] derivatives in high yields (Scheme 1).

The configuration between both rings in **4** and **6** was secured by the *endo*-transition state of the IMDA reaction. The access to the *isomeric* to **4** and **6** bicyclic derivatives (*cis*-**4** and *trans*-**6**) should be possible from the *Z*-dienoaldehyde assuming the same *endo*-mechanism of the IMDA. Recently we have found that *cis*-dienoaldehyde **8** can be prepared in high yield by thermal decomposition of secondary allyltins **7**, which were obtained (as single stereoisomers) by reaction of allylic derivatives of simple sugars with the Lipshutz reagent.[5] This compound served as a convenient synthon for the preparation of the perhydroindane system with the *cis*-junction between both rings.[6]



Scheme 1. Reagents and conditions: (i) $ZnCl_2$, CH_2Cl_2, rt, 2h; (ii) $Ph_3P{=}CHCOR$, then cyclization; (iii) (1) [O], then CH_2N_2, then $^{(-)}CH_2P(O)(OMe)_2$; (2) RCHO, K_2CO_3, 18-crown-6, toluene.

We have proven[5] that this rearrangement proceeds according to a concerted mechanism and proposed the *E*2-*anti*-elimination mode, which is consistent with that reported by Pereyre et al. for the decomposition of β-stannylalcohols[7] and β-stannylesters.[8] However,

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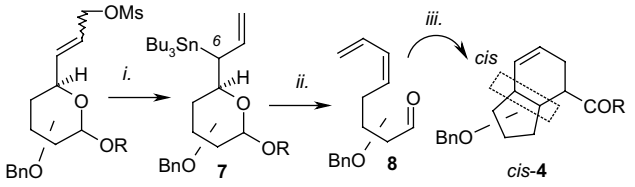
the *syn*-elimination also has to be considered and therefore proof supporting our suggestion is needed.

Another aspect that is also important is the determination of the configuration of the organotin derivatives. However, their structure can often be deduced from the products of their controlled decomposition.[9] Thus, knowledge of the mechanism of the controlled decomposition would enable the precise determination of the configuration at the stereogenic center bearing the stannyl group.

2. Results and discussion

In order to study the mechanism of the thermal decomposition of secondary sugar allylstannanes, methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-6-(tri-*n*-butylstannyl)-oct-7-eno-α-D-manno-1,5-pyranoside **9** was selected. This compound has recently been prepared by us (as single stereoisomer) in an S_N2' reaction of the corresponding primary allylic mesylate with the Lipshutz reagent (cf. Scheme 2).[5]



Scheme 2. Reagents and conditions: (i) 'Bu_3SnCu'; (ii) 140 °C; Ph_3P=CHCOR, 140 °C, Ref. 6.

Analysis of the models of thermal, controlled fragmentation of **9** (leading to *Z*-dienoaldehyde **10**) revealed that diene **10** can be formed either from the *C*-6 (*S*)-allylstannane in an *anti*-(*E*2)-mode or from the *C*-6 (*R*)-stereoisomer by the *syn*-elimination (Fig. 1). According to the stoichiometry of this rearrangement, tributyltin methoxide is eliminated.

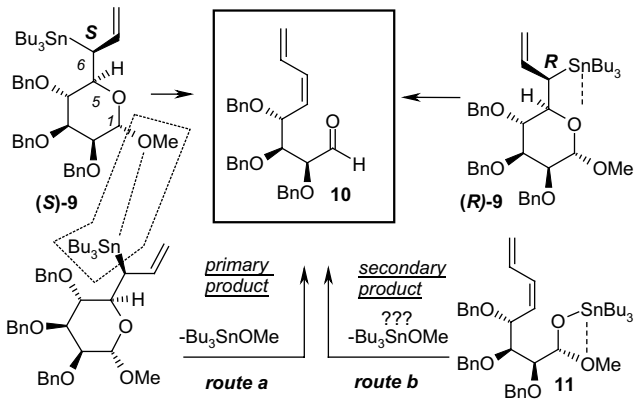
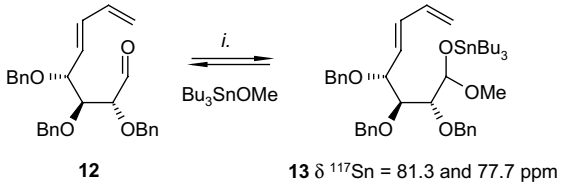


Figure 1. Possible mechanisms of decomposition of secondary allylstannanes leading to the *Z*-dienoaldehydes.

In route a, this organometallic should be formed as a primary product of the reaction, while by route b the primary product is the mixed acetal **11**, which may, eventually, decompose further with elimination of Bu_3SnOMe. The latter however is very unstable and even traces of moisture induce its decomposition to di-(tri-*n*-butyltin)oxide.[10,11]

Such mixed acetals are known, but most of them are very sensitive to moisture and readily undergo hydrolysis. Although it is claimed that adducts of aldehydes with Bu_3SnOMe (mixed acetals of type **11**) are stable to hydrolysis 'only if the carbonyl compound is a powerful acceptor (e.g., chloral)'[12] the possibility of detecting the mixed acetal by Sn NMR spectroscopy is reasonable.

In fact, the ^{117}Sn NMR spectrum of the mixture of unsaturated aldehyde **12**[13] (structurally related to **10**) and tri-*n*-butyltin methoxide showed—besides the signals for Bu_3SnOMe ($\delta = 98.5$ ppm) and $(Bu_3Sn)_2O$ (at $\delta = 83.6$; broad signal)[†]—two other resonances at $\delta = 81.3$ and 77.7 ppm, which can be connected with mixed acetal **13** (Scheme 3).



Scheme 3. Reagent and condition: (i) anhydrous xylene, 120–140 °C, 2 h.

These results indicate that the assumption of detecting the mixed acetal **11** once it has formed (even traces of it) by the Sn NMR spectroscopy is reasonable. This should enable us to distinguish between the *anti* (route a in Fig. 1) and *syn* (route b) elimination mechanisms of the thermal decomposition of secondary sugar allyltins. Assuming an *anti*-elimination (Fig. 1, route a), the formation of Bu_3SnOMe in the fragmentation of secondary sugar allyltin could be easily anticipated. This compound, as well as its decomposition product (tributyltin oxide), was readily detected by the ^{117}Sn NMR spectroscopy (see Fig. 2). Since, the mixed acetal of type **11**, can also be seen by this method, simple recording of the spectrum after decomposition conducted in dry xylene at 140 °C, should unequivocally point at the mechanism of the decomposition.

In Figure 2, a detailed study of the thermal decomposition of the secondary isomer **9** by ^{117}Sn NMR is presented. Drawing I represents three independently recorded ^{117}Sn NMR spectra of Bu_3SnOMe (95.55 ppm), $(Bu_3Sn)_2O$ (81.27 ppm; broad signal)[‡] and the secondary isomer **9** (−18.35 ppm). In II, the spectrum of the sample of Bu_3SnOMe, which was heated

[†] This product resulted from the decomposition of Bu_3SnOMe, see further text.

[‡] The chemical shift depends highly on the concentration of these species.

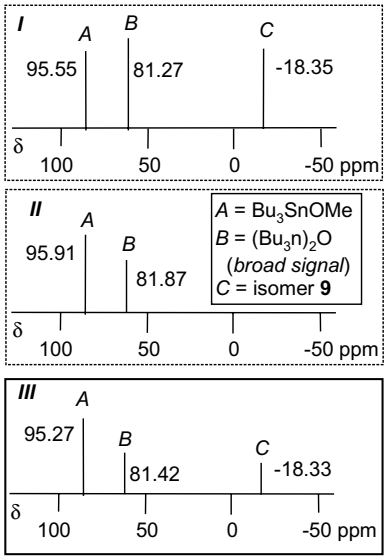


Figure 2. The ^{117}Sn NMR study of decomposition of secondary allyltin derivatives: (I) the superposition of three independent model spectra of Bu_3SnOMe (A), $(Bu_3Sn)_2O$ (B), and allyltin **9** (C); (II) spectrum after heating of Bu_3SnOMe for 1 h at 140 °C; (III) spectrum after heating of **9** for 1 h at 140 °C.

in dry xylene for 2 h at 140 °C, is shown. Substantial decomposition of the methoxytin derivative into tributyltin ether (δ_{Sn} = 81.87 ppm; broad signal)[§] was noted, which suggests that even under anhydrous conditions, tributyltin methoxide is not stable even at high temperatures. Part III in Figure 2, shows the spectrum of the sample obtained after heating of secondary isomer **9** at 140 °C for 1 h in dry xylene. It can be seen that the only compounds detected are Bu_3SnOMe (= 95.27), its decomposition product $Bu_3SnOSnBu_3$ (δ = 81.87), **9** (δ = −18.33 ppm), and the unreacted allyltin **9**. No other signals were found in the spectrum, which suggests that the mixed acetal **11** was not formed and therefore, the fragmentation of the secondary allyltin derivative **9** proceeded according to the *anti*-(*E*2)-elimination mode (Fig. 2). Furthermore although, in the post-reaction mixture (obtained after heating of **9** at 140 °C) aldehyde **10** and tributyltin methoxide appear, no formation of **11** was observed (which can be eventually formed by the addition of Bu_3SnOMe to the aldehyde as shown in Fig. 1). This is probably the result of a low concentration of Bu_3SnOMe liberated during the thermal decomposition of **9**.

The knowledge of the mechanism of thermal decomposition of **9** allowed us to assign the absolute configuration at the stereogenic center bearing the $SnBu_3$ group as (6*S*) (Fig. 1).

3. Conclusion

Thermal decomposition of secondary sugar allyltin derivatives proceeded according to the *anti*-(*E*2)-elimination mechanism as proven by the ^{117}Sn NMR spectroscopy. The knowledge of the mechanism of the thermal decomposition of such organometallics allows us to solve the very difficult problem, of determining the configuration of the stereogenic center bearing the stannyl moiety.

4. Experimental

4.1. General

The ^{117}Sn NMR spectra (in dry xylene; lock benzene-d_6) were measured at 303 K on a Bruker DRX 500 spectrometer equipped with a TBI 500SB H-C/BB-D-05 Z-G probe head, operating at 178.217 MHz. Typical conditions were as follows: 1000–2000 transients, relaxation delay 0.5 s, pulse width 4.5 μs (ca. 300), 128 K data points, spectral width 100 kHz, and power gated decoupling sequence.

4.2. Thermal rearrangement of tin derivatives

Samples of **9**, Bu_3SnOMe, and $(Bu_3Sn)_2O$ were dissolved separately in dry xylene, each at $c \sim 0.1$ M/L. The ^{117}Sn NMR spectra were recorded for each derivative at 20 °C; δ_{Sn} 95.55 (Bu_3SnOMe), 81.27 [(broad signal); $(Bu_3Sn)_2O$] and −18.35 (**9**) ppm. The data are shown in Figure 2, drawing I.

A sample of Bu_3SnOMe in dry xylene (c = 0.1 M/L) was heated under reflux under anhydrous conditions for 2 h. After cooling to room temperature, the ^{117}Sn NMR spectrum was recorded (drawing II in Fig. 1); besides the signal of tin methoxide (δ = 95.91 ppm) a tributyltin oxide signal (= 81.87 ppm; b s) was also detected.

The sample of **9** ($c \sim 0.1$ M/L) in dry xylene was heated under reflux under anhydrous conditions for 2 h. After cooling the ^{117}Sn NMR spectrum was recorded (drawing III in Fig. 1), and showed only three signals, which were assigned to Bu_3SnOMe, $(Bu_3Sn)_2O$, and **9** (at δ 95.27, 81.42, and −18.33 ppm, respectively), were detected.

4.3. NMR study of the formation of the mixed acetal 13

Aldehyde **12** (0.5 mmol) and Bu_3SnOMe (1 mmol) were dissolved in dry xylene (2 mL) and heated at 120 °C for 2 h. After this time, the mixture was cooled to room temperature, and half of this solution transferred into the NMR tube, which was dried for 30 min at 100 °C. The ^{117}Sn NMR spectrum revealed signals at δ = 83.6, 81.2, and 77.7 ppm. The signal at 83.6 was identified as $(Bu_3Sn)_2O$ by the addition of the original sample of dibutyltin ether to this solution.

Acknowledgements

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[§]It was identified precisely by addition of the original sample of $(Bu_3Sn)_2O$ to the mixture.

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