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Stereodivergent Synthesis of Iminosugars from Stannylated Derivatives of (*S*)-Vinylglycinol

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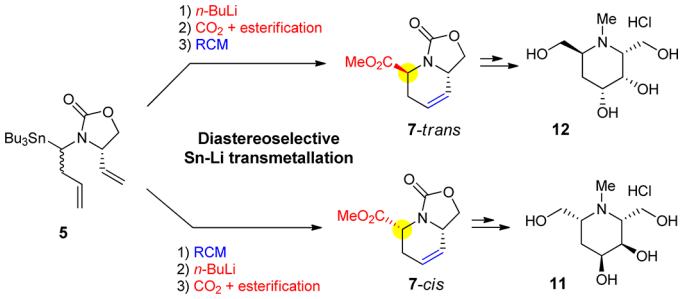
ABSTRACT



An original access to iminosugars from a *cis*/*trans* mixture of stannylated oxazolidinones 5 is reported. The dehydropiperidines 7-*trans* and 7-*cis* were obtained stereoselectively with an *RS* and *SS* configuration depending on the order of the Sn—Li transmetalation (followed by electrophilic trapping) and of the ring closing metathesis reactions due to the stereoselective epimerization of the α-aminoanion intermediate. The dehydropiperidines 7-*trans* and 7-*cis* were subsequently used for the synthesis of enantiopure homonojirimycin analogs.

Iminosugars have found widespread interest due to the biological properties of this class of compounds as glycosidases inhibitors,[1] properties which have been used for the development of treatment against viral infections such as human immunodeficiency virus (HIV), human hepatitis C or dengue virus,[2] diabetes,[3] tuberculosis,[4] cancers,[5] and lysosomal storage disorders.[6]

These important polyhydroxylated *N*-heterocycles can be obtained from natural sugars or from nonsugar compounds.[7,8] The approach starting from natural sugars allows access to well-defined molecules, but with a lower flexibility in the modifications of the parent compound,

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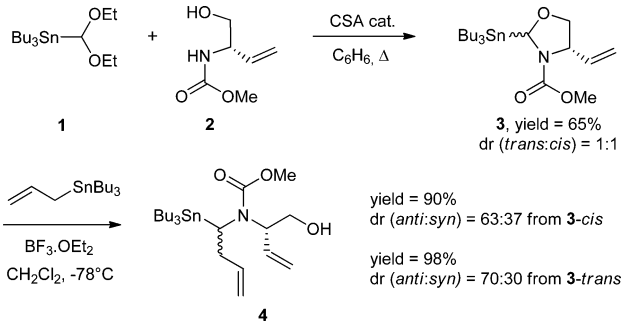
when compared to the second approach which allows for instance the preparation of eight 1-deoxynojirimycin isomers from a single precursor.[9] Among the plethora of strategies, allylmetalation of imines combined with ring closing metathesis (RCM) has also been widely used as a key step.[10] We have developed a diastereoselective route toward iminosugars based on a highly *syn*-selective allylstannation of an *N*-acyliminium intermediate by a γ-silyloxyallyltin.[11] However, while desired iminosugars were synthesized with very high diastereoselectivity, only racemic mixtures were obtained, limiting the use of this methodology for the development of new potent therapeutic agents. As part of an ongoing program to synthesize enantioenriched α-amino stannylated derivatives,[12] we report herein an original, flexible access to enantiopure iminosugars based on a diastereoselective Sn−Li transmetalation followed by electrophilic trapping of α-amino stannylated derivatives of (*S*)-*N*-methoxycarbonylvinylglycinol **2** (Scheme 1). The synthesis began with the preparation of 2-tributylstannyloxazolidine **3** *via* a transacetalization reaction[13] between diethoxymethyltributyltin **1** and **2**.

3 was obtained in good yield (65%) as a 1:1 mixture of diastereomers (**3**-*trans*/**3**-*cis*) which were separated to consider possible differences in terms of reactivity.

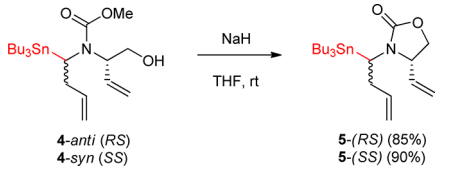
Ring opening with allyltributyltin in the presence of $BF_3 \cdot OEt_2$ at −78 °C afforded azadienol **4** in excellent yield (90 and 98% starting from **3**-*cis* or **3**-*trans* respectively), albeit giving a moderate *anti* selectivity (**4**-*anti*:**4**-*syn* = 63:37 from **3**-*cis* and 70:30 from **3**-*trans*). However, **4**-*anti* and **4**-*syn* were easily separated by column chromatography on silica gel.

Treatment of **4**-*anti* and **4**-*syn* with an excess of sodium hydride (3 equiv) furnished the desired stannylated oxazolidinones **5**-(*RS*) and **5**-(*SS*) in 85% and 90% yield respectively (Scheme 2).[14]

Scheme 1. Synthesis of Azadienols **4**-*syn* and **4**-*anti* Starting from (*S*)-*N*-Methoxycarbonyl-vinylglycinol **2**

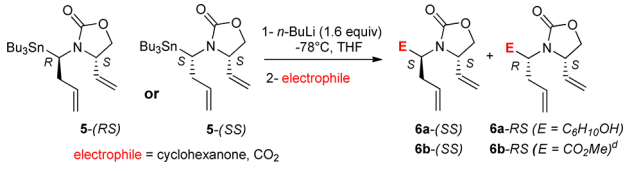


Scheme 2. Synthesis of Stannylated Oxazolidinones **5**



We then considered the Sn−Li transmetalation by *n*-BuLi at low temperature which can occur with complete retention of the configuration at the anionic center of an α-aminoorganotin precursor.[12d,15] At higher temperatures, it is also possible to take advantage of the epimerization of the anionic center to obtain the desired compounds with

Table 1. Sn−Li Transmetalation/Electrophilic Trapping Sequence on Stannylated Oxazolidinones **5**



entry	**5**	temp	electrophile	**6**	yield (*SS*:*RS*)[c]
1	**5**-(*RS*)	−78 °C	cyclohexanone[a]	**6a**	71 (100:0)
2	**5**-(*SS*)	−78 °C	cyclohexanone[a]	**6a**	47 (100:0)
3	**5**-(*SS*)	−100 °C	cyclohexanone[a]	**6a**	77 (26:74)
4	**5**-(*RS*)	−78 °C	CO_2[a]	**6b**	65 (96:4)[d]
5	**5**-(*RS*)	−78 °C	CO_2[a]	**6b**	76 (97:3)[e]
6	**5**-(*SS*)	−78 °C	CO_2[a]	**6b**	49 (95:5)[d]
7	**5**-(*SS*)	−100 °C	CO_2[b]	**6b**	78 (29:71)[d]

[a] Electrophile added 20 min after the addition of *n*-BuLi. [b] Electrophile added 5 min after the addition of *n*-BuLi. [c] Determined by GC analyses. [d] Conversion in methyl ester using $SOCl_2$/MeOH. [e] Using $TMSCHN_2$.

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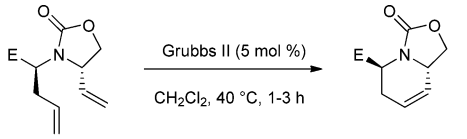
high stereoselectivities and in particular when stannylated oxazolidinones are involved.[14,15] A different situation was recently reported using α-stannylated sulfonamides with cesium fluoride at 100 °C under carbon dioxide pressure which afford products with inversion of the configuration through a tin ate complex.[16]

Transmetalation reactions of stannylated oxazolidinones **5**-(*RS*) and **5**-(*SS*) were performed at −78 or −100 °C using *n*-BuLi in THF followed by an electrophilic trapping of the corresponding anionic species by cyclohexanone or CO_2 (Table 1). When starting from **5**-(*RS*), the transmetalation followed by electrophilic trapping with cyclohexanone (after 20 min) occurred with complete retention of the configuration (entry 1) while a complete epimerization of the anionic center and a lower yield were observed with **5**-(*SS*) (entry 2).[17] This result was corroborated by a reaction at −100 °C followed by trapping after 5 min which exhibits only a partial epimerization (**6a**-(*SS*):**6a**-(*RS*) = 26:74, entry 3).

Scheme 3. Synthesis of Dehydropiperidines **7**



6a-(*SS*), E = $C_6H_{10}OH$
6b-(*SS*), E = CO_2Me

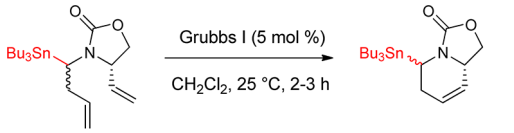
7a-*trans* (96%)
7b-*trans* (87%)

These results are in agreement with a transmetalation occurring with retention of the configuration at the anionic center at −100 °C followed by an epimerization which occurs more easily at higher temperatures (−78 °C) as already observed for this type of anions.[14,15]

Similar trends were observed when CO_2 was used as an electrophile (entry 4−7), although a slight epimerization of the stereogenic center was observed when starting from both **5**-(*RS*) and **5**-(*SS*) and whatever the esterification reaction used. After purification, diastereopure dienes **6a**-(*SS*) and **6b**-(*SS*) were then successfully transformed into their dehydropiperidine derivatives **7a**-*trans*[17] and **7b**-*trans* by RCM using the Grubbs II catalyst (Scheme 3).

At this stage, we also decided to consider the RCM performed on stannylated oxazolidinones **5** whereas only a few examples of such a reaction on stannylated oxadienes have been reported.[18] The stannylated oxazolidinones **8**-*trans* and **8**-*cis* were obtained in excellent yields (95% and 89% yield respectively) using the Grubbs I catalyst (Scheme 4).

Scheme 4. Synthesis of Bicyclic Stannylated Oxazolidinones **8**

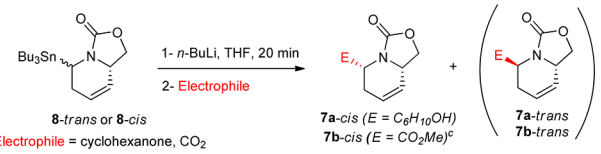


5-(*RS*) (85%)
5-(*SS*) (90%)

8-*trans* (*RS*) (95%)
8-*cis* (*SS*) (89%)

The reactivity of stannylated oxazolidinones **8** was then examined (Table 2), and contrary to the reaction carried out with **5**-(*RS*), Sn−Li transmetalation of **8**-*trans* followed by electrophilic trapping with cyclohexanone afforded pure **7a**-*cis* in 30% yield after complete epimerization of the anionic center. However, to our delight, using the same conditions, **8**-*cis* furnished exclusively **7a**-*cis* in good yield (72%).[17] The moderate yield obtained when starting from **8**-*trans* should be due to a partial decomposition of the organolithium reagent during the epimerization reaction. Similar results were obtained with CO_2 as the electrophile, and **7b**-*cis* was obtained in excellent

Table 2. Sn−Li Transmetalation/Electrophilic Trapping Sequence on Stannylated Oxazolidinones **8**



8-*trans* or **8**-*cis*
Electrophile = cyclohexanone, CO_2

7a-*cis* (E = $C_6H_{10}OH$)
7b-*cis* (E = CO_2Me)[c]

7a-*trans*
7b-*trans*

entry	8	temp	electrophile[a]	7	yield (*cis*:*trans*)[b]
1	**8**-*trans*	−78 °C	cyclohexanone	**7a**	30 (100:0)
2	**8**-*cis*	−78 °C	cyclohexanone	**7a**	72 (100:0)
3	**8**-*cis*	−78 °C	CO_2	**7b**	88 (100:0)[c]
4	**8**-*trans*	−100 °C	CO_2	**7b**	15 (100:0)[c,d]

[a] Electrophile added 20 min after the addition of *n*-BuLi. [b] Ratio determined by GC analyses. [c] The carboxylic acid was not isolated but converted into its methyl ester using trimethylsilyldiazomethane ($TMSCHN_2$). [d] Contaminated by protonated product (E = H).

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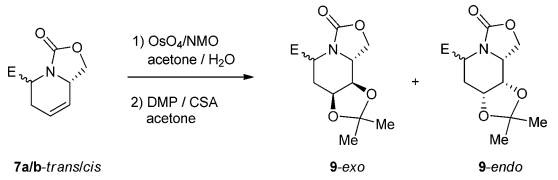
(17) The absolute configuration of this compound was confirmed by X-ray analysis.

yield (88%) as a pure diastereomer after esterification under mild conditions using trimethylsilyldiazomethane. Interestingly, complete epimerization was also observed at −100 °C (entry 4, Table 2). It is worth noting that previous reports using (−)-sparteine showed that the resulting competitive chelation of this external chiral ligand can strongly modify the stereochemical course of the reaction depending on the nature of the electrophilic trapping reagent.[19] In the present work, the configurational preference in the epimerization step (when allowed by temperature conditions) is substrate dependent and only controlled by the respective stability of the obtained intramolecularly chelated anionic species.

With compounds **7**-*trans* and **7**-*cis* in hand, their modification into iminosugars was examined through a dihydroxylation/deprotection sequence. First, the dihydroxylation was achieved with osmium tetroxide in the presence of *N*-methyl morpholine *N*-oxide[20] affording the expected diols which were subsequently converted into their acetonide derivatives **9** for easier characterization (Table 3).

Table 3. Stereoselective Dihydroxylation of **7**-*trans*/**7**-*cis*



entry	**7**	electrophile	**9**	yield (*exo*:*endo*)[a]
1	**7a**-*cis*	$C_6H_{10}OH$	**9a**-*cis*	85 (>98/2)
2	**7b**-*cis*	CO_2Me	**9b**-*cis*	79 (95/5)
3	**7a**-*trans*	$C_6H_{10}OH$	**9a**-*trans*	94 (15/85)
4	**7b**-*trans*	CO_2Me	**9b**-*trans*	78 (17/83)

[a] Ratio determined from ^{1}H NMR or by GC analyses of the crude.[21]

Good to excellent diastereoselectivities in favor of the *exo* (entries 1, 2, Table 3) or *endo* (entries 3, 4, Table 3) isomers were observed depending on the stereochemistry of the starting material (*cis* or *trans*). These stereochemical results are consistent with the structure of the dehydropiperidines **7a/b**. Indeed, in **7a/b**-*cis*, the presence of the E group ($C_6H_{10}OH$/CO_2Me) on the concave face of the bicyclic system induces a nearly exclusive approach of osmium tetroxide on the convex face, while, for **7a/b**-*trans*, the presence of the E group on the convex face allows a preferred approach of osmium tetroxide on the concave face, but with lower selectivity.[21]

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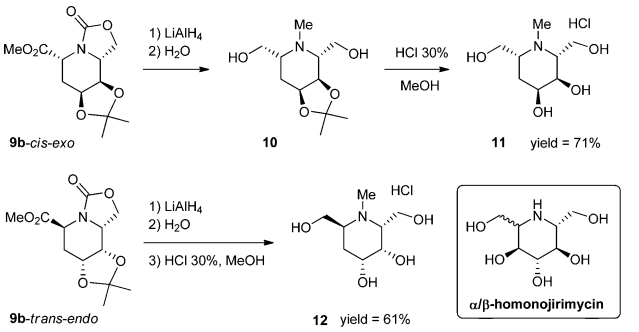
Scheme 5. Access to Homonojirimycin Analogs **11** and **12**



Compounds **9b**-*cis*-*exo* and **9b**-*trans*-*endo* were finally reduced into the corresponding *N*-methyl 2, 6-*bis*(hydroxymethyl) piperidines using lithium aluminum hydride. Subsequent acid promoted deprotection furnished 2-deoxy-*N*-methyl β-homoallonojirimycin analog **11** and 2-deoxy-*N*-methyl α-homogalactonojirimycin analog **12** (Scheme 5).

In summary, the proposed strategy constitutes an efficient, stereodivergent route toward *cis* and *trans* dehydropiperidine scaffolds (**7**-*cis*/**7**-*trans*) starting from a common key intermediate **5** by modifying the order of the transmetalation/electrophilic trapping and of the RCM reactions.

The use of the appropriate precursor, **5**-(*RS*) and **5**-(*SS*), for the preparation of **7**-*trans* and **7**-*cis* respectively led to higher yields but had no effect on the stereochemical course of the reaction. Therefore, the transmetalation/RCM (or *vice versa*) sequence can be achieved from diastereomeric mixtures of **5** or its azadienol precursor **4**. Finally, the application of this methodology to the preparation of homonojirimycin analogs (**11**/**12**) exemplified the usefulness and efficiency of this method for the stereoselective synthesis of iminosugars.

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Supporting Information Available. Experimental procedures, characterizations, and NMR spectra of the products; X-ray analysis for **6a**-(*SS*), **7a**-*cis*, **7a**-*trans*, and **9b**-*trans*-*endo*. This material is available free of charge via the Internet at http://pubs.acs.org.

(21) See Supporting Information for details and X-ray analysis of **9b**-*trans*-*endo*.

The authors declare no competing financial interest.