Identification of Chiral *cis*- and *trans*-2-Stannyloxazolidines by Their NMR Spectra and Solid-State Structures

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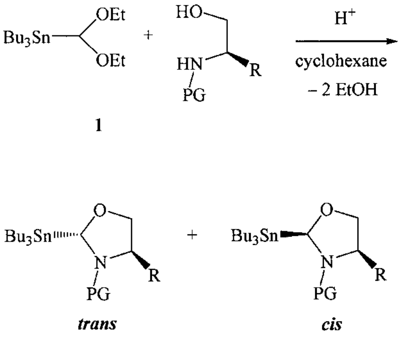
The assignment of *cis* and *trans* configurations in *N*-protected 4-substituted 2-tributylstannyl-1,3-oxazolidines by NMR has been achieved through the use of extrapolations of Karplus–Kitching-type relationships for $^{3}J(^{119}Sn–C–Z–^{13}C)$ to establish the shape of the oxazolidine ring. Examination of $^{3}J(H,H)$ allowed the determination of torsion angles for the substituents on C^{4} and C^{5}, discrimination being completed by comparison of the H^{2} chemical shifts, together with the $^{2}J(Sn–C–H^{2})$ values. The validity of the method was subsequently corroborated by comparison of the results obtained for the liquid phase with those obtained from radiocrystallographic structures of triphenylstannyl analogues or DFT calculations on trimethylstannyl analogues.

Introduction

Transacetalisation of (diethoxymethyl)tributyltin (**1**) by *N*-protected β-amino alcohols has proved to be an efficient route through which to obtain *N*-protected 2-triorganostannyl-1,3-oxazolidines.[1–5] When chiral β-amino alcohols are used, the reaction affords diastereomeric mixtures of *cis* and *trans* isomers, as defined by the relative positions of the tributylstannyl group and the R group on the newly created five-membered ring (Scheme 1).



Scheme 1. Transacetalisation of (diethoxymethyl)tributyltin (**1**) with *N*-protected (*R*)-phenylglycinol

Because of the flexibility of the oxazolidine ring, which is influenced both by the nature of the substituents and by the protective group on nitrogen, unambiguous assignment of the *cis* or *trans* configuration requires detailed NMR studies, which can be greatly facilitated by the presence of the tin nucleus. This contribution completes those devoted to the preparation of 2-tributylstannyl-1,3-oxazolidines and 2-tributylstannyl-1,3-perhydroxazines,[1] and focuses both on criteria that can allow NMR assignment of the relative configurations and on additional corroboration obtained by X-ray analyses of a *cis*/*trans* pair of (*S*)-valinol-derived 2-triphenylstannyl-1,3-oxazolidines.

Results and Discussion

NMR Assignment of the *trans* and *cis* Diastereomers

2-Tributylstannyl-1,3-oxazolidines are oily compounds, and assignment of their *trans* and *cis* structures accordingly has to be based on multinuclear NMR analysis. While chemical shifts and coupling constants between protons are generally unsuitable for unambiguous establishment of the configurations of unknown organic oxazolidines,[6] the presence of the tin nucleus brings considerable significant information with it.[7,8] For instance, ^{119}Sn chemical shifts can be obtained, and in a more efficient manner, values of $^{2}J(^{119}Sn-C-^{1}H)$, $^{1}J(^{119}Sn-^{13}C)$, $^{3}J(^{119}Sn-C-O-^{13}C)$ or $^{3}J(^{119}Sn-C-N-^{13}C)$ coupling constants would be expected to provide crucial information on the oxazolidine ring conformation. Subsequently, the configuration of each isomer should be reasonably assignable after consideration of $^{3}J(^{1}H-C-C-^{1}H)$ values[9] and nuclear Overhauser ef-

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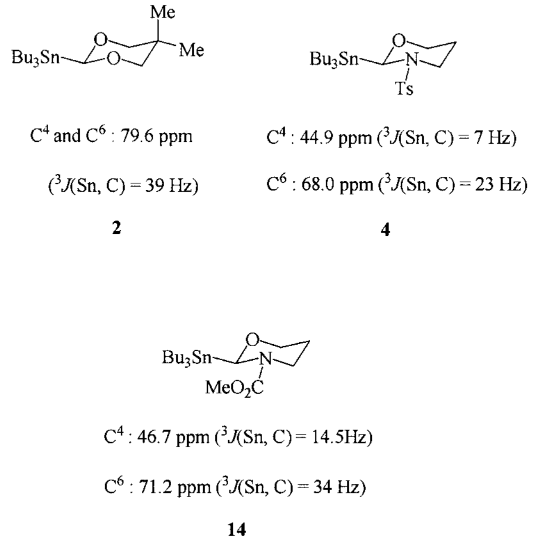
fects (NOEs). By this approach, we have successively examined *N*-sulfonylated 1,3-oxazolidines (in which the nitrogen is known to maintain a pyramidal character)[10] and *N*-alkoxycarbonylated 1,3-oxazolidines, in which the nitrogen, while flattened, also has some pyramidal character.[6] A general analysis of the potential information provided by vicinal $^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ coupling constants and by parameters that can be modified by anomeric effect was first examined.

Use of $^{3}J(^{119}\mathrm{Sn,C})$ Coupling Constants

In spite of the absence of well established Karplus-type relationships either for $^{3}J(^{119}\mathrm{Sn{-}C{-}N{-}}^{13}\mathrm{C})$ or for $^{3}J(^{119}\mathrm{Sn{-}C{-}O{-}}^{13}\mathrm{C})$, these coupling constants should be appropriate tools for investigation of the structures of stannylated heterocycles. A broad relationship between dihedral angle and $^{3}J(^{119}\mathrm{Sn{-}C{-}N(Me){-}}^{13}\mathrm{C})$ has recently been given[11] by its inclusion in the previously reported $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}}^{13}\mathrm{C})$ Kitching−Karplus curve.[12] These experimentally ascertained values appear to be far from the predicted ones when strongly withdrawing groups such as *tert*-butoxycarbonyl are present on nitrogen.[11] These Karplus-type curves are well established for $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}}^{13}\mathrm{C})$,[12−14] $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}D})$,[15] $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}}^{31}\mathrm{P})$[16] or $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}}^{119}\mathrm{Sn})$[17] in saturated systems and have been used for identification of geometrical isomers such as vinyl and dienyltins, for example.[18] When a heteroelement has been introduced into the linkage − as in $^{3}J(\mathrm{H{-}Si{-}C{-}H})$[19] or $^{3}J(^{119}\mathrm{Sn{-}Si{-}C{-}D})$,[20] for instance − the general shape of the curve has been shown or considered to be preserved, albeit with some modifications of the coupling constants, which become smaller than those observed for $^{3}J(\mathrm{H{-}C{-}C{-}H})$[9,21] or $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}D})$.[15]

Accordingly, in the present case, for a homogeneous series, a more reliable way to evaluate dihedral angles would be to examine $^{3}J(^{119}\mathrm{Sn{-}C{-}N(PG){-}}^{13}\mathrm{C})$ values (for PG = Ts and PG = $\mathrm{CO_2R}$) and $^{3}J(^{119}\mathrm{Sn{-}C{-}O{-}}^{13}\mathrm{C})$ values after measurement of these ^{3}J values in compounds with a dihedral angle close to 180° (*anti* relationship). As these curves are likely to follow Karplus-type variations as a function of the relative spatial orientation of Sn and Cγ, these experimentally determined values for a 180° dihedral angle should reflect the modification of the electron spin density by the presence of the heteroatom in the linkage with subsequent effects on the $^{3}J(\mathrm{Sn, C})$ values. We therefore considered 5,5-dimethyl-2-tributylstannyl-1,3-dioxane (**2**)[22] as a model for an evaluation of $^{3}J(^{119}\mathrm{Sn{-}C{-}O{-}}^{13}\mathrm{C})$ for 180°, while the perhydroxazines **4** and **14** described in the accompanying paper,[1] (in order to help the reader, the compound numbers **1−31** used in the accompanying paper have been kept in this article.[1]) can be regarded as appropriate models showing more accurate values for $^{3}J(^{119}\mathrm{Sn{-}C{-}O{-}}^{13}\mathrm{C})$ and $^{3}J(^{119}\mathrm{Sn{-}C{-}N(PG){-}}^{13}\mathrm{C})$ in structures close to *N*-protected 2-tributylstannyl-1,3-oxazolidines (Scheme 2).



C^4 and C^6 : 79.6 ppm ($^{3}J(\mathrm{Sn, C}) = 39$ Hz)

2

C^4 : 44.9 ppm ($^{3}J(\mathrm{Sn, C}) = 7$ Hz)

C^6 : 68.0 ppm ($^{3}J(\mathrm{Sn, C}) = 23$ Hz)

4

C^4 : 46.7 ppm ($^{3}J(\mathrm{Sn, C}) = 14.5$Hz)

C^6 : 71.2 ppm ($^{3}J(\mathrm{Sn, C}) = 34$ Hz)

14

Scheme 2. $^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ values in 2-tributylstannyl-acetals and 2-tributylstannyl-1,3-perhydroxazines

From the data presented in Scheme 2, a value of approximately 35−40 Hz can reasonably be assigned from **2** for $^{3}J(^{119}\mathrm{Sn\ {-}C{-}O{-}}^{13}\mathrm{C})$ with θ = 180°, a value in agreement with that observed for $^{3}J(^{119}\mathrm{Sn{-}C{-}S{-}}^{13}\mathrm{C})$ (32.4 Hz) in *trans*-5-*tert*-butyl-2-trimethylstannyl-1,3-dithiane.[23] Evaluation of $^{3}J(^{119}\mathrm{Sn{-}C{-}N(PG){-}}^{13}\mathrm{C})$ for θ = 180° is much more tedious, due to steric interactions or chelation effects that are capable of inducing distortion in the six-membered ring. Given a value near 40 Hz for $^{3}J(^{119}\mathrm{Sn{-}C{-}O{-}}^{13}\mathrm{C})$ (θ = 180°), maximal values of about 13 Hz can reasonably be evaluated for $^{3}J(\mathrm{Sn{-}C{-}N(PG){-}C})$ with θ = 180° in *N*-Ts derivatives and about 16 Hz in *N*-$\mathrm{CO_2R}$ derivatives, if account is made for the distortions occurring for both Sn−C−O−C and Sn−C−N(PG)−C in 2-tributylstannyl-1,3-perhydroxazines. The $^{3}J(^{119}\mathrm{Sn{-}C{-}O{-}}^{13}\mathrm{C})$ value of 23 Hz in **4** indicates a dihedral angle of under 180° (about 150°), probably due to the steric hindrance between the tributylstannyl group and the tosyl group with concomitant effects on the dihedral angle Sn−C−N−C, which can be broadly evaluated as around 140°. The observed $^{3}J(^{119}\mathrm{Sn{-}C{-}N{-}}^{13}\mathrm{C})$ value of 7 Hz for 140° allows a $^{3}J(^{119}\mathrm{Sn{-}C{-}N{-}}^{13}\mathrm{C})$ value of around 12−13 Hz to be predicted for θ = 180°. In the *N*−$\mathrm{CO_2R}$ derivative **14**, the $^{3}J(^{119}\mathrm{Sn{-}C{-}O{-}}^{13}\mathrm{C})$ value of 34 Hz indicates smaller distortion, which might reflect partial compensation of the steric effect by a chelation effect between the tributylstannyl group and the alkoxycarbonyl group. With a value of 34 Hz for $^{3}J(^{119}\mathrm{Sn{-}C{-}O{-}}^{13}\mathrm{C})$, the dihedral angle can be evaluated as 160−170° with a concomitant effect for the dihedral angle Sn−C−N−C, which is likely to be around 160°, indicating a value of around 16 Hz for θ = 180°. Using these evaluated $^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ values and considering the well established Karplus−Kitching relationship for $^{3}J(^{119}\mathrm{Sn{-}C{-}C{-}}^{13}\mathrm{C})$,[12,13] we took the risk of extrapolating the general shape of this curve to the series of $^{3}J(^{119}\mathrm{Sn{-}C{-}Z{-}}^{13}\mathrm{C})$ values obtained for Z = O, Z = N−Ts or Z = N−$\mathrm{CO_2R}$ (Figure 1) by using a single point

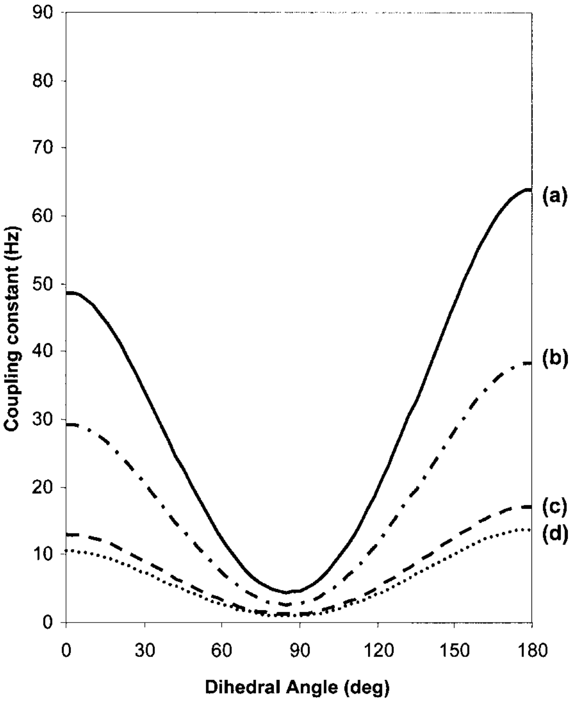


Figure 1. Extrapolated Kitching−Karplus-type relationships for $^{3}J(^{119}Sn-C-Z-^{13}C)$ as a function of the dihedral angle in tributylstannyl derivatives. (a) Kitching−Karplus relationship for $^{3}J(^{119}Sn-C-C-^{13}C)$ as a function of the dihedral angle.[12,13] (b) Extrapolated curve for $^{3}J(^{119}Sn-C-O-^{13}C)$. (c) Extrapolated curve for $^{3}J(^{119}Sn-C-N(CO_2R)-^{13}C)$. (d) Extrapolated curve for $^{3}J(^{119}Sn-C-N(Ts)-^{13}C)$.

in each case and assuming a similar monotonous effect of the heteroatom along the curve, as already observed for ^{3}J(H−Si−C−H) in relation to ^{3}J(H−C−C−H).[19] It is worth noting that the $^{3}J(^{119}Sn-C-C-^{13}C)$ Karplus−Kitching relationship has been established from trimethylstannyl derivatives.[12,13] This means that a similar curve with a decrease in values of coupling constants by about 10−15% should be observed in tributylstannyl series if one refers to the effect of substituents on tin for $^{3}J(^{119}Sn-C-C-^{13}C)$[24,25] or $^{3}J(^{119}Sn-C-C-D)$ values.[15,26,27] The effect of *N*(PG) in the transmission of couplings for $^{3}J(^{119}Sn-C-N(PG)-^{13}C)$ can be broadly taken into account with this type of evaluation. The observation of a ^{3}J value of 11.8 Hz made recently by Gawley for a 120° dihedral angle in a Sn−C−N−C linkage is not in good agreement with these curves, but it should be taken into account that this observation was made on a strained isoquinuclidine skeleton with subsequent alteration of the electron density due to a modification of the *s* character of the bonding.[11]

Use of δ H^{2}, $^{2}J(^{119}Sn,H)$, $^{1}J(^{119}Sn,C)$ and δ^{119}Sn

Even if not fully reliable because of the flexibility of the oxazolidine ring, the hydrogen atom at the 2-position would be expected to appear at a higher field when located in an antiperiplanar position relative to the pseudoaxial lone pairs on both oxygen and nitrogen atoms.[28,29] The conformation of the oxazolidine ring can be strongly modified by the nature of the substituents, however, and the H^{2} chemical shift cannot be considered alone but with regard to $^{1}J(^{119}Sn-^{13}C)$ and $^{2}J(^{119}Sn-C-^{1}H)$. This last value (usually positive in tetraorganostannanes and dependent on the spin densities) should decrease as the Sn−C−H^{2} angle is increasing.[8] The NMR spectroscopic data for unsubstituted 2-stannyloxazolidines **3** and **13** (analogues of perhydroxazines **4** and **14**) in *N*-Ts and *N*-CO$_2$Me derivatives, respectively, are given in Table 2 and Table 3 for comparison, as examples of more flexible systems. The last available parameter, the ^{119}Sn chemical shift, though highly sensitive for discrimination between very similar organostannanes,[15,26,30] is almost useless for primary identification because of its extreme sensitivity to steric effects,[27] to solvation and to chelation effects.[31]

Assignment of the Configurations of 3-Sulfonylated 2-Tributylstannyl-1,3-oxazolidines 6−12

A detailed study has been devoted to (*R*)-*N*-Ts-phenylglycinol-derived oxazolidines in order to discriminate between the *cis* isomer and the *trans* isomer by consideration of both configurational and conformational aspects. Discrimination between *cis* and *trans* configurations was established from ^{1}H NMR spectra, especially from the observation of proximity interactions through NOESY studies (Table 1).

On the basis of these measurements, the **6-*trans*** configuration was assigned to the first eluted (TLC; silica gel with hexanes/ethyl acetate, 95:5 as eluent) isomer and **6-*cis*** to the second. Furthermore, consideration of $^{n}J(^{119}Sn,^{13}C)$ in the ^{13}C NMR spectra together with the above results allowed evaluation of the distortion of the oxazolidine cycle and of its preferred conformation for each isomer.

It might be noted that the pseudo-axial positions of the 2- and 4-substituents are in agreement with Seebach's observations for purely organic *N*-acyloxazolidines.[6] The importance of the Ts group on nitrogen is also underlined, as it interacts both with the tributylstannyl group and the phenyl group in the *trans* isomer (dihedral angles near 60°), while the *cis* configuration allows a decompression effect (dihedral angles about 120° with tributylstannyl and phenyl substituents), which explains the higher stability of the *cis* isomer in compound **6**.[1] Similar principles might also apply for other diastereomer pairs. Discrimination between *cis* and *trans* isomers for compounds **6**−**12** on the basis of significant NMR parameters such as H^{2} chemical shifts, $^{2}J(^{119}Sn-C-H^{2})$, $^{1}J(^{119}Sn-^{13}C^{2})$, $^{3}J(^{119}Sn-C-N-^{13}C^{4})$, $^{3}J(^{119}Sn-C-O-^{13}C^{5})$ and ^{119}Sn chemical shifts thus appeared possible. The convergence of these meaningful values is in agreement with the corresponding *trans* and *cis* assignment given for compounds **6**−**9**, **11** and **12** (Table 2).

Larger values of ^{2}J(Sn,H), together with larger $^{1}J(^{117,119}Sn-C)$ coupling constants, for instance, were observed for the *cis* isomers than for the *trans* isomers.

Table 1. Main discriminative NMR spectroscopic data allowing assignment of the configurations of the **6-*trans*** and **6-*cis*** diastereomers in their more favoured conformations

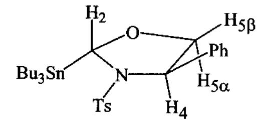
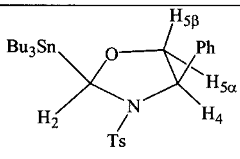
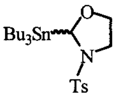
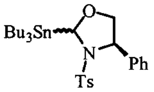
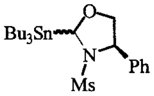
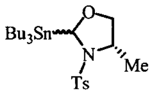
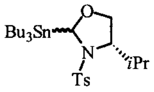
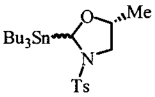
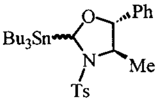
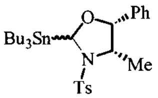
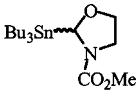
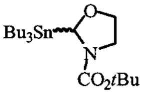
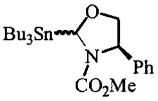
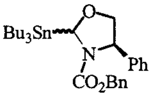
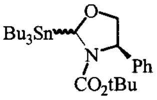
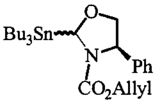
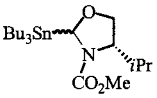
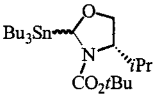
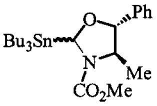
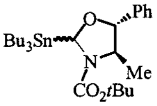
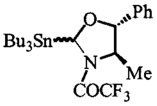
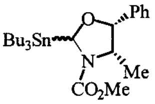
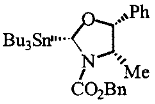
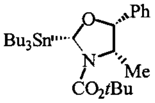
Compound	First eluted isomer: **6-*trans***		Second eluted isomer: **6-*cis***	
Meaningful NMR data	^{1}H NMR: • H^2 (δ = 4.83 ppm, ^2J(Sn,H) = 27.6 Hz) has strong interactions with H^{5β} and Ph, weak interactions with the Ts group and no interaction with H^4. • H^4 (δ = 4.85 ppm, ^3J(H,H) = 6.0 Hz, ^3J(H,H) = 7.3 Hz) has strong interactions with H^{5α} and Ph, weak interactions with H^{5β} and Ts group and no interaction with H^2. • H^{5α} (δ = 4.37 ppm, ^3J(H,H) = 7.3 Hz, $\|^2J$(H,H)$\|$ = 8.3 Hz) has interactions with H^4 and H^{5β} but no interaction with Ph. • H^{5β} (δ = 3.69 ppm, ^3J(H,H) = 6.0 Hz, $\|^2J$(H, H)$\|$ = 8.3 Hz) has strong interactions with H^2, H^{5α} and Ph, weak interactions with H^4. ^{13}C NMR: δ = 89.5 (C^2, ^1J(Sn,C) = 308/323 Hz); 75.8 (C^5, ^3J(Sn,C) = 33.8 Hz); 62.1 (C^4, ^3J(Sn,C) = 10.5 Hz). ^{119}Sn NMR: δ = –36.8 ppm.		^{1}H NMR: • H^2 (δ = 5.26 ppm, ^2J(Sn,H) = 57.2 Hz) has strong interactions with H^{5α} and Ts group and weak interactions with H^4. • H^4 (δ = 4.62 ppm, ^3J(H, H) = 3.2 Hz, ^3J(H,H) = 6.6 Hz) has interactions with H^2, H^{5α}, H^{5β}, Ph, and Ts group. • H^{5α} (δ = 3.50 ppm, ^3J(H,H) = 6.6 Hz, $\|^2J$(H,H)$\|$ = 8.6 Hz) has strong interactions with H^2, H^4 and H^{5β} but no interaction with Ph. • H^{5β} (δ = 3.90 ppm, ^3J(H,H) = 3.2 Hz, $\|^2J$(H,H)$\|$ = 8.6 Hz) has strong interactions with H^{5α} and Ph, weak interactions with H^4. ^{13}C NMR: δ = 91.5 (C^2, ^1J(Sn,C) = 380/402 Hz); 74.9 (C^5, ^3J(Sn,C) = 21.9 Hz) ; 61.5 (C^4,^3J(Sn,C) = 7.2 Hz). ^{119}Sn NMR: δ = –34.8 ppm.	
Major conformation	 **6-*trans***		 **6-*cis***	
Dihedral angles evaluation	Coupling constants (Hz)	Evaluated dihedral angles (°)	Coupling constants (Hz)	Evaluated dihedral angles (°)
	^3J(Sn, C^4) = 10.5	Sn–C–N–C ~ 170	^3J(Sn,C^4) = 7.2	Sn–C–N–C ~ 130
	^3J(Sn, C^5) = 33.8	Sn–C–O–C ~ 170	^3J(Sn,C^5) = 21.9	Sn–C–O–C ~ 130
	^3J(H^4,H^{5α}) = 7.3	H^4–C–C–H^{5α} ~ 10	^3J(H^4,H^{5α}) = 6.6	H^4–C–C–H^{5α} ~ 15
	^3J(H^4,H^{5β}) = 6.0	H^4–C–C–H^{5β} ~ 130	^3J(H^4,H^{5β}) = 3.2	H^4–C–C–H^{5β} ~ 105

Table 2. Characterisation of 3-sulfonyl-2-tributylstannyl-1,3-oxazolidines through NMR parameters

Compound[a]		^{1}H NMR		^{13}C NMR		^{119}Sn
		δ H^2 ($\|^2J$(Sn,H)$\|$)[b]	δ C^2 (^1J(Sn,C))[b]	δ C^4 (^3J(Sn,C))[b]	δ C^5 (^3J(Sn,C))[b]	δ Sn
3		5.36 (48.5)	89.7 (390/408)	46.9 (6.8)	66.2 (14.5)	–33.2
6-*trans*		4.83 (27.6)	89.5 (308/323)	62.1 (10.5)	75.8 (33.8)	–36.8
6-*cis*		5.26 (57.2)	91.5 (380/402)	61.5 (7.2)	74.9 (21.9)	–34.8
7-*trans*		4.59 (14.6)	89.0 (284/298)	61.85 (12.6)	75.5 (34.3)	–37.1
7-*cis*		5.38 (50.6)	91.4 (375/392)	61.4 (7.6)	75.8 (21.3)	–32.1
8-*trans*		4.52 (18.3)	86.0[c]	54.4[c]	74.4 (34.0)	–38.3
8-*cis*		5.00 (62.5)	90.5 (397/416)	54.4[c]	74.1 (21.3)	–33.2
9-*trans*		4.38 (9.6)	87.4 (310/323)	64.6[c]	69.4 (35)	–40.0
9-*cis*		4.90 (59.8)	90.5 (400/418)	64.3 (8.4)	69.5 (23.6)	–32.2
10-*trans*		5.61 (44.6)	89.9 (394/413)	52.9[c]	74.3 (10.3)	–33.4
10-*cis*		5.12 (62/64)	90.1 (397/415)	53.4 (9.0)	74.7 (20.2)	–33.4
11-*trans*		4.82 (17.2)	87.3 (298/312)	62.8 (11.4)	91.1 (37.9)	–36.7
11-*cis*		5.90 (42.6)	90.7 (404/423)	62.0[c]	87.7[c]	–35.8
12-*cis*		5.03 (66.7/69.4)	89.4 (389/410)	57.8 (10.2)	83.8 (25.6)	–29.5

[a] The *trans*/*cis* nomenclature refers to the relative positions of the tributylstannyl group and of the R group at the 4-position; in compound **10** the methyl group in the 5-position is considered. [b] J values are given in Hz. [c] The coupling constant was not determined, due either to low resolution (^3J(Sn,C) < 7 Hz) or to an insufficiently good signal/noise ratio.

Table 3. NMR characterisation of 3-alkoxy-2-tributylstannyl-1,3-oxazolidines **18**−**29**

Compound[a]	Structure	^{1}H NMR	^{13}C NMR			^{119}Sn[c]
		δ H^2 (^2J(Sn,H))[b]	δ C^2 (^1J(Sn,C))[b]	δ C^4 (^3J(Sn,C))[b]	δ C^5 (^3J(Sn, C))[b]	δ Sn
13		4.8 (71.4)	87.7 (397/415)	43.2[c]	68.7 (32.4)	−38.4, −32.8
16		5.09 (70.9)	88.5 (398/416)	45.7 (8.4)	69.6 (31.3)	−43.5
18-*trans*		5.37 (60.4/63.1)	89.9 (376/394)	60.8 (8)	77.0 (27.5)	−42.6, −31.8
18-*cis*		5.21 (69.4/72.3)	89.5 (404/422)	59.8 (10.3)	76.9 (35.5)	−39.0, −34.5
19-*trans*		5.38 (61.4)	89.8 (373/391)	60.7 (8)	77.1 (29)	−41.5
19-*cis*		5.22 (68/71)	89.4 (398/416)	59.9 (10)	77.0 (32)	−39.1
20-*trans*		5.37 (61.6)	88.8 (382/400)	60.5 (9.1)	77.4 (34.3)	−40.1
20-*cis*		5.27 (66.9)	89.6 (409/428)	59.9 (10.2)	77.3 (37.3)	−43.3
21-*trans*		5.37 (60.7/62.8)	90.0 (369–386)	60.9 (9.1)	77.3 (32.8)	−43.8
21-*cis*		5.25 (68.5/71.7)	89.5 (400–414)	59.9 (9.8)	77 (nd)	−40.5
22-*trans*		4.96 (61.5)	88.5(389/407)	61.7 (7)	69.8 (28.6)	−42.3, −31.8
22-*cis*		5.08 (72.6/75.6)	89.2 (428/448)	61.9 (10.6)	70.8 (35.1)	−38.7, −35.3
23-*trans*		4.90 (64)	88.1 (397/416)	61.7[d]	70.1 (30.3)	−47.4, −37.0
23-*cis*		5.09 (74.3/77)	89.5 (418/436)	61.7[d]	70.9 (34)	−40.0, −37.0
24-*trans*		5.17 (54.6/57.2)	87.3 (371/389)	60.1 (10.7)	90.4 (38.5)	−43.8
24-*cis*		5.74 (75/78)	88.0 (423/442)	57.9[d]	87.6 (19.1)	−40.5
25-*trans*		5.26 (54.4/56.7)	87.1 (380/397)	60.5 (10.7)	90.5 (40.4)	−47.5
25-*cis*		5.94 (72/75)	87.8 or 88.3[c]	57.9[d]	87.8 or 88.3[c]	−40.8
26-*trans*		5.06 (43)	88.1 (329/344)	60.2[d][e]	90.7 (32.4)	−35.0, −32.7
27-*trans*		5.83 (79/82.8)	89.2 (411/430)	56.5[d]	83.5 (< 10)	−37.6
27-*cis*		5.34 (76.3)	87.9 (397/417)	55.4[d]	85.2 (28.2)	−36.6, −32.8
28-*cis*		5.47 (71.3/74.6)	87.9 (399/420)	55.6[d]	85.3 (28.6)	−36.2, −32.1
29-*cis*		5.35 (74.9/78.7)	87.6 (424/438)	55.0[d]	85.0 (28)	−36.3, −31.5

[a] The *trans*/*cis* nomenclature refers to the relative positions of the tributylstannyl group and of the R group on the 4-position. [b] *J* values are given in Hz. [c] When two values are mentioned they correspond to two conformers, the relative abundances of which are given in the Exp. Sect. of the accompanying paper.[d] The coupling constant was not determined, due either to low resolution [$^3J(^{119}Sn-C-N-^{13}C$ and $^3J(^{119}Sn-C-O-^{13}C) < 7$ Hz] or to an insufficiently good signal/noise ratio. [e] $^1J(^{13}C,^{19}F) = 2.3$ Hz

The sole case in which these parameters were not convergent was that of compound **10** (unsubstituted on the 4-position), but in this case the more stable conformation might be that with the 5-methyl substituent in a pseudo-axial position, with a decrease of ^{3}J(Sn,C) in the *trans* isomer (θ ≈ 120° instead of 170°). Accordingly, although not definitively pointed out, the *minor* isomer is believed to remain **10-*trans***.

Assignment of the Configurations of 3-Alkoxycarbonyl-2-tributylstannyl-1,3-oxazolidines and Related Species 18−29

The NMR spectra recorded at room temperature were hardly usable in these series, due to slow equilibria between conformers, which appear to be mainly due to rotation of the carbonyl group on the nitrogen atom, since ^{2}J(Sn,H^{2}) remains virtually independent of the temperature, consistently with minor fluctuations of the geometry at the level of the oxazolidine ring. Accordingly, the spectra were subsequently recorded at higher temperature (T = 340 K) in C_6D_6 as solvent. Under such experimental conditions, fast equilibria (at NMR time scales) occurred, and well resolved signals provided a complete set of experimental data both in the ^{1}H and in the ^{13}C NMR spectra. Meaningful NMR parameters for compounds **18−29** are reported in Table 3.

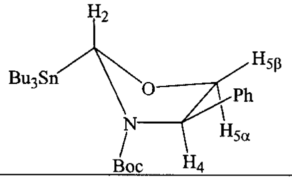
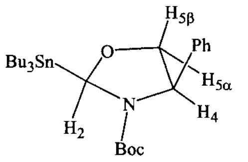
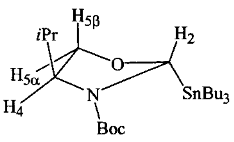
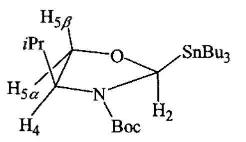
By consideration of the previously discussed criteria [δ H^{2}, ^{2}J(^{119}Sn,H), ^{1}J(^{119}Sn,^{13}C), ^{3}J(^{119}Sn,^{13}C) and ^{3}J(H^{4},H^{5})], the more favourable conformations of (*R*)-phenylglycinol- and (*S*)-valinol-derived 2-stannyloxazolidines **20** and **23** can be proposed on the basis of the observed values to be close to those given in Table 4.

Through the use of the meaningful signals and coupling constant values discussed above, the assignment of the *cis* or *trans* configurations can be achieved unambiguously for compounds **18** to **29** (Table 3). In line with Colombo's reports,[2] *cis* configurations were assigned to the major or exclusive compounds for the (1*R*,2*S*-norephedrine-derived oxazolidines (compounds **27−29**). This assignment was confirmed for **28**, which was shown to be *cis* by NOE experiments (strong H^{2}/H^{5} and H^{4}/H^{5} interactions and a weak interaction between H^{2} and H^{4}). In this series, the Sn−C−*N*−C, Sn−C−O−C and H^{4}−C−C−H^{5} dihedral angles can be evaluated from the ^{3}J(^{119}Sn,^{13}C) and ^{3}J(H,H) values as about 120°, 120° and 15°, respectively, for the *trans* isomers, and about 140°, 150°, and 15°, respectively, for the *cis* isomers. The assignment of the *cis* and *trans* configurations for derivatives of (1*R*,2*R*)-norpseudoephedrine was firmly established from NOE experiments for compound **24**, obtained as mixture of diastereomers. Subsequently, the *trans* (or *cis*) configurations of compounds **25** and **26** were assigned on the basis of δ H^{2}, ^{3}J(^{119}Sn,^{13}C) and ^{3}J(H,H), broad evaluations of the Sn−C−*N*−C, Sn−C−O−C and H−C^{4}−C^{5}−H dihedral angles being about 140°, 150° and 140°, respectively, for the *trans* isomer and 130°, 140° and 110°, respectively, for the *cis* isomer.

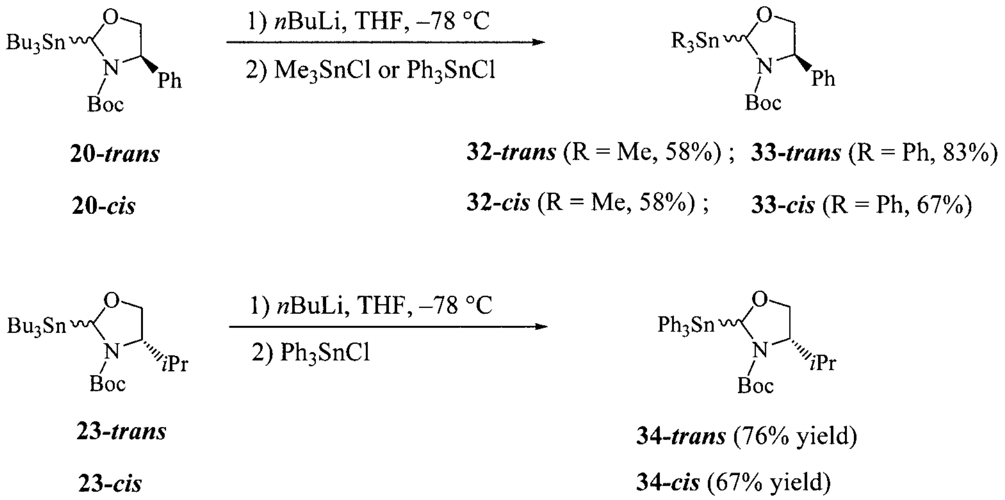
Transmetallation of 2-Tributylstannyl-1,3-oxazolidines

When we first developed an interest in this field,[32] several contributions from Colombo's group[2−4] demonstrated the possibility of transmetallation of (1*R*,2*S*)-*N*-Boc-norephedrine- and camphor-derived 2-tributylstannyl-1,3-oxazolidines. In both cases, however, the transmetallation was carried out only on the *cis* isomers, and so cannot be regarded as conclusive for the configurational stabilities of the anions in these series, since *cis* lithio derivatives might have similar preferences in terms of thermodynamic stability. Accordingly, several experiments were attempted separately for the *cis* and *trans* isomers of (*S*)-valinol- and (*R*)-phenylglycinol-derived oxazolidines (compounds **20** and **23**) in order to provide an unambiguous answer to this question.[5] For *N*-Ts derivatives, transmetallation by *n*-butyllithium in THF was proved to be possible, but further

Table 4. Proposed structures for **20-*trans***, **20-*cis***, **23-*trans*** and **23-*cis***

	Compounds (represented in their deduced conformations)			
2-(Tributylstannyl)-1,3-oxazolidines				
No.	**20-*trans***	**20-*cis***	**23-*trans***	**23-*cis***
	Coupling constants (Hz) / Evaluated dihedral angles (deg)			
^{3}J(Sn,C^{4}) / Sn–C–N–C	9.1 / ~ 150	10.2 / ~ 160	< 7.0 / ~ 140	8.8 / ~ 150
^{3}J(Sn,C^{5}) / Sn–C–O–C	34.3 / ~ 160	37.3 / ~ 170	30.3 / ~ 160	34 / ~ 160
^{3}J(H^{4},H$^{5\alpha}$) / H^{4}–C–C–H$^{5\alpha}$	7.3 / ~ 10	6.5 / ~ 20	6.3 / ~ 10	6.3 / ~ 20
^{3}J(H^{4},H$^{5\beta}$) / H^{4}–C–C–H$^{5\beta}$	8.4 / ~ 130	2.0 / ~ 100	5.2 / ~ 130	1.0 / ~ 100
	NOE experiments[a]			
	- H^{2} with H$^{5\beta}$ - H^{2} with Ph (H^{ortho}) - H^{4} and H$^{5\alpha}$	- H^{2} with H$^{5\alpha}$ (s) - H^{2} with H^{4} (w) - H$^{5\alpha}$ with H^{2}, H^{4}, H$^{5\beta}$	- H^{2} with H$^{5\beta}$ and *i*Pr (Me) - H^{4} with H$^{5\alpha}$ (s), *i*Pr (CH and one Me) (s), H$^{5\beta}$ (w) and *t*Bu - H$^{5\beta}$ with H^{2} (s), H$^{5\alpha}$ (s) and H^{4} (w)	- H^{2} with H$^{5\alpha}$ (s) - H^{2} with H^{4} (w) - H^{4} with H$^{5\alpha}$ - H^{4} with *i*Pr and H^{2} - H$^{5\beta}$ with H$^{5\alpha}$ (s) and *i*Pr

[a] (s) indicates a strong interaction, (w) indicates a weak interaction.



Scheme 3. Transmetallation of 3-(*tert*-butoxycarbonyl)-2-tributylstannyl-1,3-oxazolidines with *n*-butyllithium

degradation occurred even at −100 °C, prohibiting examination of the configurational stabilities of the 2-lithio-3-tosyl-1,3-oxazolidines. In *N*-Boc derivatives, the expected reactions took place, and trapping with triphenylstannyl or trimethylstannyl halides unambiguously demonstrated the configurational stability of the 2-lithio-1,3-oxazolidinyl anion at −78 °C over 30 min (Scheme 3).

Through the obtaining of 2-trimethylstannyl- and 2-triphenylstannyl-1,3-oxazolidines, the stereochemistry of the reaction can be easily checked through the use of the NMR criteria described above [δH^2, $^3J(^{119}Sn,^{13}C)$, $^3J(H,H)$] for assignment of *cis* or *trans* configurations (Table 5) if allowance is made for the fact that the $^3J(^{119}Sn,^{13}C)$ values would be expected to be increased by about 10−15% in trimethylstannyl derivatives and by 20−25% in triphenylstannyl derivatives for similar dihedral angles with regard to tributylstannyl derivatives and $^3J(^{119}Sn-C-C-^{13}C)$ values[24,25] or $^3J(^{119}Sn-C-C-D)$ values.[15,26,27]

Furthermore, suitable crystals for X-ray analyses of 2-triphenylstannyl-1,3-oxazolidines **34-*trans*** and **34-*cis*** were obtained, and their ORTEP views are given below (Figure 2 and Figure 3), while crystal and refinement data for both compounds are reported in Table 6. The *cis* and *trans* configurations of these two diastereomers were determined unambiguously, and furthermore, the absolute configuration (already known) was also confirmed from the Flack parameter.

The obtained information on the configurations and conformations of this pair of diastereomers was compared with the evaluations obtained from NMR spectra (Table 7). In the information provided by X-ray analyses, the chelation occurring between the carbonyl group and the tin atom should be underlined. While single van der Waals contact should give Sn−O^1 bond lengths of 3.51 Å, the observed values for Sn−O^1 are 2.76 Å for **34-*trans*** and 3.34 Å for **34-*cis***. These values are indicative of stronger chelation be-

Table 5. Characterisation of 2-trimethylstannyl- and 2-triphenylstannyl-1,3-oxazolidines **32**, **33** and **34** through meaningful NMR parameters and comparison with those of **20** and **23**

Compound[a]	^{1}H NMR			^{13}C NMR[b]		
	$^3J(H^4,H^{5\alpha})$[b]	$^3J(H^4,H^{5\beta})$[b]	δ H^2 ($\lvert ^2J(Sn,H)\rvert$)[b]	δ C^2 [$^1J(Sn,C)$][b]	δ C^4 [$^3J(Sn,C)$][b]	δ C^5 [$^3J(Sn,C)$][b]
20-*trans* (Bu_3Sn)	7.3	8.4	5.37 (61.6)	88.8 (382/400)	60.5 (9.1)	77.4 (34.3)
20-*cis* (Bu_3Sn)	6.5	2.0	5.27 (66.9)	89.6 (409/428)	59.9 (10.2)	77.3 (37.3)
23-*trans* (Bu_3Sn)	6.3	5.2	4.90 (64.0)	88.1 (397/416)	61.7 (nd)	70.1 (30.3)
23-*cis* (Bu_3Sn)	6.3	1.0	5.09 (74.3/77.0)	89.5 (436)	61.7 (nd)	70.9 (34)
32-*trans* (Me_3Sn)	7.2	7.2	5.19 (69.1)	89.3 (457/479)	61.2 (11)	77.6 (39)
32-*cis* (Me_3Sn)	6.3	2.0	5.05 (75.0)	88.2 (329/346)	59.7 (12)	77.8 (39)
33-*trans* (Ph_3Sn)	7.1	7.0	5.91 (83.0/87.0)	90.3 (535/559)	60.2 (12)	77.4 (37)
33-*cis* (Ph_3Sn)	6.9	2.5	5.78 (88.0/93.0)	91.1 (557/583)	60.0 (13)	77.4 (45)
34-*trans* (Ph_3Sn)	6.2	5.4	5.51 (80.0/83.0)	90.7 (547/573)	62.8 (10.3)	71.5 (34.7)
34-*cis* (Ph_3Sn)	6.2	1.2	5.72 (96.0/100)	91.7 (589/618)	61.8 (14.0)	71.6 (41.2)

[a] The *trans*/*cis* nomenclature relates to the positions of the 4-substituent and the tributylstannyl group. [b] *J* values are given in Hz.

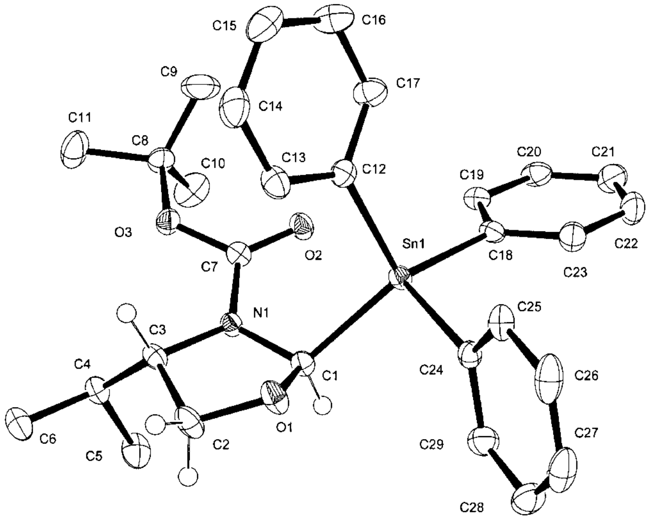


Figure 2. ORTEP view of compound **34-*trans*** with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms other than those of the oxazolidine ring are omitted for clarity

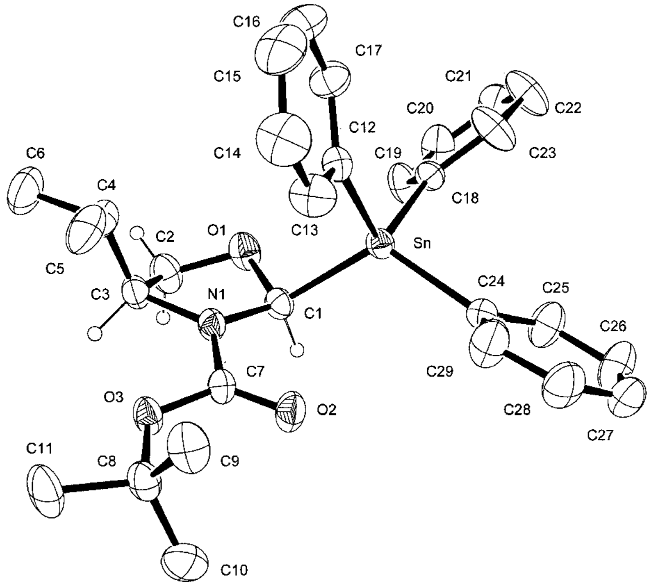


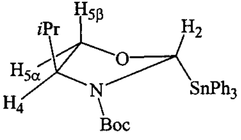
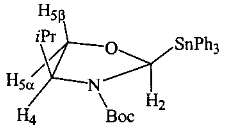
Figure 3. ORTEP view of compound **34-*cis*** with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms other than those of the oxazolidine ring are omitted for clarity

Table 6. Crystal and refinement data for **34-*trans*** and **34-*cis***

	34-*cis*	**34-*trans***
Empirical formula	$C_{29}H_{35}NO_3Sn$	$C_{29}H_{35}NO_3Sn$
Molecular mass	564.30	564.27
Temperature (K)	294	293(2)
Diffractometer	CAD4	KappaCCD
Wavelength (Å)	0.70926	0.71069
Crystal size	0.22 × 0.25 × 0.35	0.45 × 0.25 × 0.25
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.599(7)	10.2599(10)
b (Å)	15.013(2)	14.8100(10)
c (Å)	18.959(3)	18.1162(2)
Volume (Å^3)	2732(2)	2752.74(4)
Z	4	4
Density (calculated) (Mg·m^{-3})	1.372	1.362
Absorption coefficient (mm^{-1})	0.964	0.956
F(000)	1160	1160
θ range for data collection (deg)	1.73 to 26.99	2.41 to 27.49
Index ranges		
h	0 to 12	−13 to 13
k	0 to 19	−19 to 19
l	0 to 24	−23 to 23
Reflections collected	3344	6308
Independent reflections	3344 [*R*(int) = 0.0000]	6308 [*R*(int) = 0.0000]
Reflections observed [$I > 2\sigma(I)$]	3152	6242
Data completeness	0.999	0.999
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3152/1/308	6308/0/308
Goodness-of-fit on F^2	1.047	1.100
Final *R* int [$I > 2\sigma(I)$]	R1[a] = 0.0238, *wR*2[b] = 0.0634	R1[a] = 0.0158, *wR*2[b] = 0.0416
R int (all data)	R1[a] = 0.0277, *wR*2[b] = 0.0650	R1[a] = 0.0161, *wR*2[b] = 0.0418
Absolute structure parameter	0.06(3)	−0.013(10)
Flack parameter	0.06	0.0(1)
Extinction coefficient	0.003(4)	0.0061(3)
Largest diff. peak and hole (e·Å^{-3})	0.936 and −0.597	0.459 and −0.440

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o)^2 + (uP)^2 + vP]$ where $P = (F_o^2 + 2F_c^2)/3$, $u = 0.051$ and $v = 0.202$; for **34-*cis*** and $u = 0.0221$ and $v = 0.5820$ for **34-*trans***.

Table 7. Comparison of the dihedral angles obtained by NMR evaluation, by solid-state measurement and by DFT calculations

2-(Triphenylstannyl)-1,3-oxazolidine	Dihedral angle	^3J (Hz) / estimated dihedral angle value (deg)[a]	Measured angle (deg) on solid state	Calculated angle (deg) on full optimised geometry[b]
 **34-*trans***	Sn–C–O–C	34.7 / 150	153.7	165.0
	Sn–C–N–C	10.3 / 140	132.7	147.0
	H^4–C–C–$H^{5\alpha}$	6.2 / 20	27.3	18.1
	H^4–C–C–$H^{5\beta}$	5.4 / 140	147.5	142.1
 **34-*cis***	Sn–C–O–C	41.2 / 170	154.5	156.2
	Sn–C–N–C	14 / 150	125.7	129.5
	H^4–C–C–$H^{5\alpha}$	6.2 / 30	29.6	31.7
	H^4–C–C–$H^{5\beta}$	1.2 / 90	91.6	94.1

[a] The evaluation was carried out with allowance being made for an increase of about 20−25% in the ^3J(Sn,C) values when triphenylstannyl derivatives rather than tributylstannyl derivatives are involved.[25] [b] DFT calculations were performed on trimethylstannyl derivatives.

tween tin and carbonyl group in the *trans* isomer (in relation to the *cis* isomer) in these derivatives. More interestingly, we were delighted to see that dihedral angles determined in the solid state are close to those obtained from NMR evaluation (Table 7).

The obtained NMR evaluations, which may include contributions from minor conformers in addition to that of the major one, due to possible flexibility of the heterocycle in solution, can be considered to be in good agreement with those determined in the solid state. Accordingly, this radiocrystallographic analysis constitutes corroboration of the previously used NMR determination. Furthermore, DFT calculations performed on trimethylstannyl analogues (in order to simplify the calculations) were also in good agreement with the experimentally obtained values.

These observations constitute a posteriori validation of the broad evaluation carried out for $^3J(^{119}Sn-C-O-^{13}C)$ and $^3J(^{119}Sn-C-N-^{13}C)$ in NMR studies.

Conclusion

The *cis* or *trans* configurations of 4-substituted 2-triorganostannyl-1,3-oxazolidines were assigned through careful NMR study of these compounds. The main tools allowing the assignment were the consideration of modified Karplus−Kitching relationships for $^3J(^{119}Sn-C-O-^{13}C)$ and $^3J(^{113}Sn-C-N(PG)-^{13}C)$. Through the use of the values of these coupling constants, the shape of the oxazolidine ring can be broadly determined, and consideration of the ^3J(H−C−C−H) values allows broad evaluation of the torsions arising in the five-membered ring. Obviously, additional information such as the chemical shift of H^2, measurement of $^2J(^{119}Sn-C-H)$ or $^1J(^{119}Sn-^{13}C)$ and NOE experiments was also used and has contributed to unambiguous characterisation.

Upon transmetallation with *n*BuLi (−78 °C, THF, 30 min), the title (*R*)-phenylglycinol- or (*S*)-valinol-derived 2-tributylstannyl-1,3-oxazolidines afforded 2-lithio-1,3-oxazolidines, which were trapped with trimethylstannyl or triphenylstannyl chloride to afford the expected 2-trimethylstannyl- or 2-triphenylstannyl-1,3-oxazolidines with complete retention of the configuration.

The radiocrystallographic analyses of *cis*- and *trans*-2-triphenylstannyl-1,3-oxazolidines derived from (*S*)-*N*-Boc-valinol, as well as DFT calculations from trimethylstannyl analogues, provided further information concerning intramolecular chelation between the tin centre and the carbonyl of the carbamate group and furthermore corroborates information obtained from NMR spectroscopy.

Experimental Section

General Remarks: ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded with Bruker AC 200, Bruker Avance 300 or Bruker ARX 400 spectrometers. Chemical shifts are given in ppm as δ values relative to tetramethylsilane (^1H, ^{13}C) or tetramethylstannane (^{119}Sn) and coupling constants are given in Hz ($CDCl_3$ was used as solvent at 300 K unless stated otherwise). For NOE experiments, the relaxation delay and the mixing time were 3 s and 2.8 s, respectively. Mass spectra were obtained in EI mode (70 eV) with a HP apparatus (5989A) in direct introduction mode. Organostannyl fragments are given for ^{120}Sn, which means that the given abundance are broadly one third of the overall abundance of the organostannyl fragments relative to organic ones. HRMS were recorded at the CRUS in Rouen (Centre Régional Universitaire de Spectroscopie de l′Université de Rouen). IR spectra were recorded with a Bruker IFS Vector 22 apparatus. Optical rotations were measured with a Perkin−Elmer 341 apparatus. Elemental analyses were performed by the CNRS microanalysis centre (Vernaison). Diethyl ether and THF were distilled from sodium-benzophenone prior to use. Liquid chromatography separations were carried out on Merck silica gel (Geduran Si 60, 40−63 mesh), TLC analyses on silica-coated plates (Merck Kieselgel $60F_{254}$) and HPLC analyses on a Chrompack column (Chromsep Inertsil 5 Si, 250 × 3 mm) on a HPLC chromatograph (HP series 1100), with UV detection at 254 nm.

Preparation of the 2-Tributylstannyl-1,3-oxazolidines and 2-Tributylstannyl-1,3-perhydroxazines 3−29: The compounds were prepared from (diethoxymethyl)tributylstannane[33,34] by transacetalisation with *N*-protected amino alcohols as described in the accompanying paper.[1]

Preparation of 2-Trimethylstannyl- and 2-Triphenylstannyl-1,3-oxazolidines 32−34

These compounds were prepared by transmetallation of the corresponding *3-tert*-butoxycarbonyl-2-tributylstannyl-1,3-oxazolidines with *n*-butyllithium[5] by the following experimental procedure.
A solution of *3*-(*tert*-butoxycarbonyl)-2-tributylstannyl-1,3-oxazolidine [**20-*cis***, **20-*trans*** (539 mg, 1 mmol) or **23-*cis*** or **23-*trans*** (519 mg, 1 mmol)] in THF (20 mL) was cooled to −78 °C and degassed before dropwise addition of *n*-butyllithium (1.2 mmol, 0.80 mL, 1.5 M in hexane). After the mixture had been stirred for 30 min, a solution of trimethylstannyl chloride (219 mg, 1.1 mmol) or triphenylstannyl chloride (424 mg, 1.1 mmol) was added dropwise at −78 °C. After 30 min additional stirring, hydrolysis was achieved with aqueous NH_4Cl solution. The products were subsequently extracted with diethyl ether (2 × 50 mL), and the organic layer was dried on magnesium sulfate. After filtration and evaporation of the solvent, the crude compounds were purified on silica gel (eluent: hexanes/diethyl ether/Et_3N, 95:3:2 for **32**, 70:28:2 for **33**) to afford 239 mg (58%) of **32-*trans***, 239 mg (58%) of **32-*cis***, 497 mg (83%) of **33-*trans***, or 401 mg (67%) of **33-*cis***. The crude compounds **34** were purified on silica gel (eluent: hexane/ethyl acetate, 70:30) and recrystallised from pentane/ethanol to afford 429 mg (76%) of **34-*trans*** and 379 mg (67%) of **34-*cis***.

Physicochemical Data for Compounds 32−34

(4*R*)-3-(*tert*-Butoxycarbonyl)-4-phenyl-2-trimethylstannyl-1,3-oxazolidine (32): IR: $\tilde{\nu}$ = 2972, 2907, 2842, 1805, 1648, 1398, 1157, 750 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 342 (5), 312 (7), 165 (32); organic fragments: *m*/*z* (%) = 248 (11), 192 (70), 148 (63), 120 (43), 104 (20), 57 (100), 41 (21), 29 (10). $C_{17}H_{23}NO_3Sn$ (412.1): calcd. C 49.55, H 6.60, N 3.40; found C 49.60, H 6.77, N 3.61.

32-*trans*: (58% Yield, 240 mg). ^{1}H NMR (C_6D_6, 340 K): δ = 0.44 [s, ^2J(Sn,H) = 53.0−55.0 Hz, 9 H, $(CH_3)_3Sn$], 1.18 [s, 9 H, $(CH_3)_3$], 3.53 [dd, ^2J(H,H) = 8.7, ^3J(H,H) = 7.2 Hz, 1 H, OCH_2], 4.14 [dd, ^2J(H,H) = 8.7, ^3J(H,H) = 7.2 Hz, 1 H, OCH_2], 4.57 [t, ^3J(H,H) = 7.2 Hz, 1 H, NCH], 5.19 [s, ^2J(Sn,H) = 69.1 Hz, 1 H, SnCH], 7.0−7.2 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 300 K): δ = −8.4 [^1J(Sn,C) = 336−351 Hz, 3 C, $(CH_3)_3Sn$], 28.2 [3 C, $(\mathit{C}H_3)_3C$], 61.2 [^3J(Sn,C) = 11 Hz, 1 C, NCH], 77.6 [^3J(Sn,C)= 39 Hz, 1 C, OCH_2], 79.7 [1 C, $(CH_3)_3\mathit{C}$], 89.3 [^1J(Sn,C) = 457−479 Hz, 1 C, SnCH], 126.7 (2 C, C_6H_5), 127.4 (1 C, C_6H_5), 128.5 (2 C, C_6H_5), 142.5 (1 C, C_6H_5), 152.1 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −25.4 ppm. $[\alpha]_D^{19}$ = −140.5 (*c* = 1.1 in $CHCl_3$).

32-*cis*: (58% Yield, 239 mg). ^{1}H NMR (C_6D_6, 300 K): δ = 0.36 [s, ^2J(Sn,H) = 54 Hz, 9 H, $(CH_3)_3Sn$], 1.22 [s, 9 H, $(CH_3)_3$], 3.68 [dd, ^2J(H,H) = 8.3, ^3J(H,H) = 6.3 Hz, 1 H, OCH_2], 3.89 [dd, ^2J(H,H) = 8.3, ^3J(H,H) = 2 Hz, 1 H, OCH_2], 4.43 [dd, ^3J(H,H) = 6.3, ^3J(H,H) = 2 Hz, 1 H, NCH], 5.05 [s, ^2J(Sn,H) = 75 Hz, 1 H, SnCH], 7.0−7.2 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (C_6D_6, 300 K): δ = −8.6 [^1J(Sn,C) = 343 Hz, 3 C, $(CH_3)_3Sn$], 28.0 [3 C, $(\mathit{C}H_3)_3C$], 59.7 [^3J(Sn,C) = 12 Hz, 1 C, NCH], 77.8 [^3J(Sn,C) = 39 Hz, 1 C, OCH_2], 79.3 [1 C, $(CH_3)_3\mathit{C}$], 88.2 [^1J(Sn,C) = 329−346 Hz, 1 C, SnCH], 126.5 (2 C, C_6H_5), 127.2 (1 C, C_6H_5), 128.3 (2 C, C_6H_5), 143.6 (1 C, C_6H_5), 152.1 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 340 K): δ = −23.8 ppm. $[\alpha]_D^{19}$ = +33.6 (*c* = 0.9 in $CHCl_3$).

(4*R*)-3-(*tert*-Butoxycarbonyl)-4-phenyl-2-triphenylstannyl-1,3-oxazolidine (33): IR: $\tilde{\nu}$ = 1669, 1480, 1454, 1408, 1165, 731, 695 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 498 (3), 466 (1), 351 (28), 197 (20); organic fragments: *m*/*z* (%) = 248 (38), 192 (90), 148 (100), 120 (51), 57 (100), 41 (16), 20 (6). $C_{32}H_{33}NO_3Sn$ (598.3): calcd. C 64.24, H 5.56, N 2.34; found C 63.97, H 5.58, N 2.10.

33-*trans*: (83% Yield, 495 mg). ^{1}H NMR ($CDCl_3$, 300 K): δ = 1.16 [s, 9 H, $(CH_3)_3$], 3.97 [dd, ^2J(H,H) = 8.7, ^3J(H,H) = 7.1 Hz, 1 H, OCH_2], 4.61 [dd, ^2J(H,H) = 8.7, ^3J(H,H) = 7.0 Hz, 1 H, OCH_2], 4.75 [dd, ^3J(H,H) = 7.0, ^3J(H,H) = 7.1 Hz, 1 H, NCH], 5.91 [s, ^2J(Sn,H) = 83−87 Hz, 1 H, SnCH], 7.15−7.32 (m, 14 H, C_6H_5), 7.62 [m, ^3J(Sn,H) = 45 Hz, 6 H, C_6H_5] ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 27.8 [3 C, $(CH_3)_3$], 60.2 [^3J(Sn,C) = 12 Hz, 1 C, NCH], 77.4 [^3J(Sn,C) = 37 Hz, 1 C, OCH_2], 84.8 [1 C, $(CH_3)_3\mathit{C}$], 90.3 [^1J(Sn,C) = 535−559 Hz, 1 C, SnCH], 126.4 (2 C, C_6H_5), 127.3 (1 C, C_6H_5), 128.1 [^3J(Sn,C) = 54 Hz, 6 C, C_6H_5], 128.5 (3 C, C_6H_5), 128.6 (2 C, C_6H_5), 137.4 [^2J(Sn,C) = 37 Hz, 6 C, C_6H_5], 140.2 [^1J(Sn,C) = 500−523 Hz, 3 C, C_6H_5], 140.9 (1 C, C_6H_5), 153.2 (1 C, CO) ppm. ^{119}Sn NMR (C_6D_6, 300 K): δ = −161.5 ppm. $[\alpha]_D^{19}$ = −136.5 (*c* = 0.86 in $CHCl_3$).

33-*cis*: (67% Yield, 400 mg). ^{1}H NMR ($CDCl_3$, 300 K): δ = 1.18 [s, 9 H, $(CH_3)_3$], 3.82 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 6.9 Hz, 1 H, OCH_2], 3.97 [dd, ^2J(H,H) = 8.5, ^3J(H,H) = 2.5 Hz, 1 H, OCH_2], 4.55 [dd, ^3J(H,H) = 2.5, ^3J(H,H) = 6.9 Hz, 1 H, NCH], 5.78 [s, ^2J(Sn,H) = 88−93 Hz, 1 H, SnCH], 7.1−7.4 (m, 14 H, C_6H_5), 8.0 (m, 6 H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$, 300 K): δ = 28.4 [3 C, $(CH_3)_3$], 60.0 [^3J(Sn,C) = 13 Hz, 1 C, NCH], 77.4 [^3J(Sn,C) = 45 Hz, 1 C, OCH_2], 79.2 [1 C, $(CH_3)_3\mathit{C}$], 91.1 [^1J(Sn,C) = 557−583 Hz, 1 C, SnCH], 127.2−129.4 (14 C, C_6H_5), 138.4 [^2J(Sn,C) = 36 Hz, 6 C, C_6H_5], 140.5 [^1J(Sn−C) = 502−520 Hz, 3 C, C_6H_5], 142.4 (1 C, C_6H_5), 152.7 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −158.7 (90%) and −136.2 (10%) ppm. $[\alpha]_D^{19}$ = +40.2 (*c* = 1.06 in $CHCl_3$).

(4*S*)-3-(*tert*-Butoxycarbonyl)-4-isopropyl-2-triphenylstannyl-1,3-oxazolidine (34): IR: $\tilde{\nu}$ = 2972, 2907, 2842, 1805, 1648, 1398, 1157, 750 cm^{-1}. MS: organostannyl fragments: *m*/*z* (%) = 464 (1), 351 (10), 197 (22), 121 (10); organic fragments: *m*/*z* (%) = 214 (22), 158 (100), 120 (3), 114 (60), 94 (13), 91 (78), 77 (13), 65 (8), 55 (12), 51 (9), 45 (37), 43 (12). HRMS (CI, isobutane): calcd. for $C_{29}H_{36}NO_3Sn$ [M + H$^+$] 566.1717, found 566.1713.

34-*trans*: (76% Yield, 429 mg). ^{1}H NMR (C_6D_6, 340 K): δ = 0.79 [d, ^3J(H,H) = 7 Hz, 3 H, $CH(\mathit{C}H_3)_2$], 0.83 [d, ^3J(H,H) = 7.2 Hz, 3 H, $CH(\mathit{C}H_3)_2$], 1.25 [s, 9 H, $(CH_3)_3$], 1.92 [m, $C\mathit{H}(CH_3)_2$], 3.59 [dd, ^3J(H,H) = 5.4, ^2J(H,H) = 8 Hz, 1 H, OCH_2], 3.6 (m, 1 H, NCH), 3.87 [dd, ^3J(H,H) = 6.2, ^2J(H,H) = 8 Hz, 1 H, OCH_2], 5.51 [s, ^2J(Sn,H) = 80−83 Hz, 1 H, SnCH], 7.2−7.4 (m, 9 H, C_6H_5), 7.95 [m, ^3J(Sn,H) = 47 Hz, 6 H, C_6H_5] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 18.5 [1 C, $CH(\mathit{C}H_3)_2$], 20.2 [1 C, $CH(\mathit{C}H_3)_2$], 29.2 [3 C, $(\mathit{C}H_3)_3C$], 32.0 [1 C, $\mathit{C}H(CH_3)_2$], 62.8 [^3J(Sn,C) = 10.3 Hz, 1 C, NCH], 71.5 [^3J(Sn,C) = 34.7 Hz, 1 C, OCH_2], 81.6 [1 C, $(CH_3)_3\mathit{C}$], 90.7 [^1J(Sn,C) = 547−573 Hz, 1 C, SnCH], 129.5 [^3J(Sn,C) = 55 Hz, 6 C, C_6H_5], 129.8 (3 C, C_6H_5), 138.8 [^2J(Sn,C) = 36.2 Hz, 6 C, C_6H_5], 142.6 [^1J(Sn,C) = 499−528 Hz, 3 C, C_6H_5], 155.8 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −167 ppm. $[\alpha]_D^{19}$ = +48.3 (*c* = 0.93 in $CHCl_3$).

34-*cis*: (67% Yield, 378 mg). ^{1}H NMR (C_6D_6, 340 K): δ = 0.75 [d, ^3J(H,H) = 6.8 Hz, 3 H, $CH(\mathit{C}H_3)_2$], 0.78 [d, ^3J(H,H) = 6.8 Hz, 3 H, $CH(\mathit{C}H_3)_2$], 1.41 [s, 9 H, $(CH_3)_3$], 1.88 [m, 1 H, $C\mathit{H}(CH_3)_2$], 3.50 [dd, ^3J(H,H) = 6.2, ^2J(H,H) = 8.6 Hz, 1 H, OCH_2], 3.57 (m, 1 H, NCH), 3.93 [dd, ^3J(H,H) = 1.2, ^2J(H,H) = 8.6 Hz, 1 H, OCH_2], 5.72 [s, ^2J(Sn,H) = 96−100 Hz, 1 H, SnCH], 7.25−7.37 (m, 9 H, C_6H_5), 7.96 [m, ^3J(Sn,H) = 46 Hz, 6 H, C_6H_5] ppm. ^{13}C NMR (C_6D_6, 340 K): δ = 18.4 [1 C, $CH(\mathit{C}H_3)_2$], 19.7 [1 C, $CH(\mathit{C}H_3)_2$], 28.6 [3 C, $(CH_3)_3C$], 31.2 [1 C, $CH(CH_3)_2$], 61.8 [^3J(Sn,C) = 14 Hz, 1 C, NCH], 71.6 [^3J(Sn,C) = 41.2 Hz, 1 C, OCH_2], 80.1 [$(CH_3)_3C$], 91.7 [^1J(Sn,C) = 589−618 Hz, 1 C, SnCH], 128.6 [^3J(Sn,C) = 48.5−50.7 Hz, 6 C, C_6H_5], 129.1 [^4J(Sn,C) = 11.4 Hz, 3 C, C_6H_5], 138.2 [^2J(Sn,C) = 34.5−35.9 Hz, 6 C, C_6H_5], 140.0 [^1J(Sn,C) = 480−502 Hz, 3 C, C_6H_5], 153.2 (1 C, CO) ppm. ^{119}Sn NMR ($CDCl_3$, 300 K): δ = −188.6 ppm. $[\alpha]_D^{19}$ = −133.9 (*c* = 1.06 in $CHCl_3$).

X-ray Crystal Structure Analysis of 34-*cis*: Single crystals of the compound ***34-cis*** were prepared by slow evaporation of a diethyl ether solution at room temperature. X-ray data were collected on a CAD4 ENRAF−NONIUS automatic diffractometer with the use of graphite monochromatized Mo-K_α radiation. Pertinent data for the structure determination are collected in Table 6. The cell parameters were obtained by fitting of a set of 25 high-theta reflections. After Lorenz and polarization corrections, the structure was solved by Direct Methods, which revealed all the non-hydrogen atoms in the structure. After isotropic (R = 0.085) and then anisotropic refinement (R = 0.052), many hydrogen atoms were found with a Fourier Difference between 0.94 and 0.38 e·Å^{-3}, the remaining ones being set in geometrical positions. The whole structure was refined by full-matrix, least-square techniques (use of F magnitude; x, y, z, β_{ij} for Sn, O, N and C atoms and x, y, z for some H atoms (phenyl and methyl hydrogen atoms are fixed). Absolute structure from refinement of the η parameter to 1.0(2). As a check, a refinement fixed as the opposite absolute structure gave R = 0.0273, R_w = 0.0299 and S_w = 1.347. Neutral atom scattering factors were taken from the International Tables for X-ray Crystallography.[35] The calculations were performed on a Hewlett−Packard 9000−710 for structure determination[36] and on a Digital MicroVAX 3100 computer with the MOLEN package[37] for refinement and ORTEP calculations.[38]

X-ray Crystal Structure Analysis of 34-*trans*: Single crystals of the compound ***34-trans*** were prepared by slow evaporation of a C_6D_6 solution at room temperature. The sample was studied on a NONIUS Kappa CCD with the use of graphite-monochromated Mo-K_α radiation.[39] Pertinent data for the structure determination are collected in Table 6. The cell parameters were obtained with Denzo and Scalepack[40] with 10 frames (psi rotation: 1° per frame). The structure was solved with SIR-97,[41] which revealed the non-hydrogen atoms of the structure. Subsequent anisotropic refinement was done with SHELXL-97,[42] by full-matrix, least-square techniques (use of F square magnitude; x, y, z, β_{ij} for Sn, O, C and N atoms, x, y, z in riding mode for H atoms). The value of the Flack parameter [−0.0(1)] unambiguously confirms the absolute configuration. Neutral atom scattering factors were taken from the International Tables for X-ray Crystallography.[43] ORTEP views were obtained with ORTEP III software.[38]

CCDC-231314 (**34-*cis***) and CCDC-231315 (**34-*trans***) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

DFT Calculations: All calculations were performed by use of the Gaussian98 program.[44] Calculations of energetics and geometry optimizations were carried out at the B3LYP level of theory, which consists of a hybrid Becke + Hartree−Fock exchange and a Lee−Yang−Parr correlation functional with nonlocal corrections.[45,46] The basis set used for the optimization is the LANL2DZ level for all atoms, H, C, O, N and Sn. Energies include zero-point energy (ZPE) correction. Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies.

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