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1,2-Stereoinduction in the asymmetric hydrostannation of (*E*)- and (*Z*)-trisubstituted ethylenes with (−)-menthyldimethyltin hydride

S.D. Mandolesi [1], L.C. Koll, J.C. Podestá[1] *

Departamento de Química e Ing. Química, Instituto de Investigaciones en Química Orgánica, Universidad Nacional del Sur, Avenida Alem 1253, 8000 Bahía Blanca, Argentina

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Abstract

Free radical hydrostannation of methyl (**2**) and (−)-menthyl (**3**) (*E*)-2,3-diphenylpropenoates and (*Z*)-2,3-diphenylpropenenitrile with (−)-menthyldimethyltin hydride (**1**) takes place with high diastereoselectivity. The observed 1,2-stereoinduction is explained taking into account that the combination of both allylic strain effects and the hyperconjugation existing between the β-trialkyltin substituent and the half filled carbon p orbital leads to particularly stable conformations in the intermediate radicals. These results, together with those reported earlier, indicate that it is possible to predict the stereochemistry of the hydrostannation products by considering the type of substituents attached to the olefinic bond and the preferred conformation of the intermediate radicals resulting from the addition of the organotin radical. These studies also demonstrate that it is possible to achieve asymmetric hydrostannations using organotin hydrides with chiral organic ligands. Full ^{1}H-, ^{13}C-, and ^{119}Sn-NMR data of the new organotin adducts are given. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organotin hydrides; Radical additions; 1,2-Asymmetric induction

1. Introduction

Hydrostannation of olefins provides a versatile method for the synthesis of organotin compounds containing a broad variety of functional groups. Previous studies on the addition of achiral organotin hydrides to both achiral [1] and chiral [2] activated alkenes show that these reactions take place with a high degree of stereoselectivity. More recently [3], we have shown that the observed 1,2-asymmetric induction could be connected with the existence of preferred conformations in the intermediate radicals arising from both A-strain effects and the hyperconjugative interaction that exists between the β-trialkylstannyl substituent and the half-filled carbon p orbital.

In the present paper we wish to report the results obtained in the free radical addition of chiral (−)-menthyldimethyltin hydride (**1**) to methyl and (−)-menthyl (*E*)-2,3-diphenylpropenoates (**2** and **3**, respectively) and to (*Z*)-2,3-diphenylpropenenitrile (**4**). These studies were carried out with the aim to determine the effect of: (a) the geometry of the starting olefin and (b) the α-substituents in the intermediate alkyl radicals on the stereochemistry of these reactions as well as to find out whether an organotin hydride with chiral organic ligands would be a useful reagent for asymmetric hydrostannations.

2. Results and discussion

The addition under free radical conditions of (−)-menthyldimethyltin hydride (**1**) to both methyl (**2**) and (−)-menthyl (*E*)-1,2-diphenylpropenoate (**3**) leads to mixtures of the four expected diastereoisomers, as shown in Scheme 1. The analysis by ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectroscopy of the crude products obtained in both reactions shows that each product consists of mixtures of four diastereoisomers, two of which are obtained in higher yield (ca. 91.5%, mixtures **6** + **6′** and **8** + **8′**, Scheme 1).

Although we were not able to separate these diastereomeric mixtures by column chromatography

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* Corresponding author. Fax: + 54-291-4595187.

E-mail address: jpodesta@criba.edu.ar (J.C. Podestá[1])

[1] Member of CONICET, Argentina.

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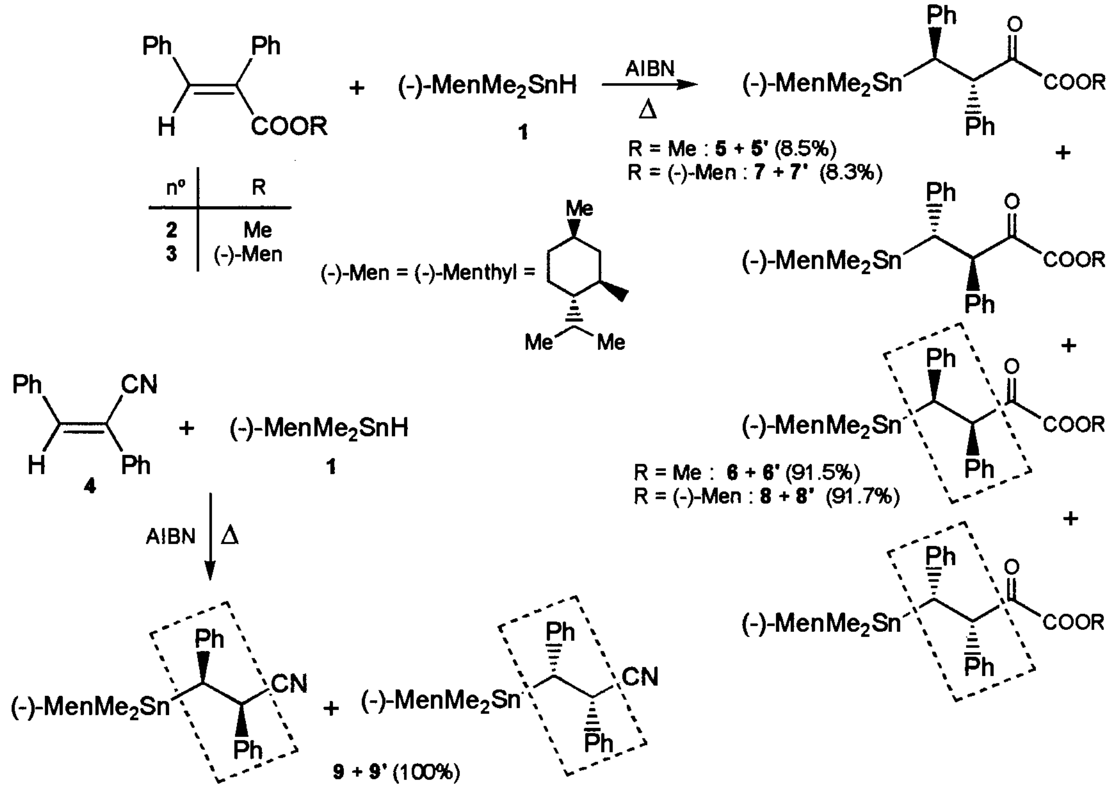
(Silica Gel 60), this method enabled us to obtain fractions containing mixtures of the stereoisomers produced in higher yield, **6** + **6**′ and **8** + **8**′ and fractions containing the stereoisomers formed in lower yield (mixtures **5** + **5**′ and **7** + **7**′) as shown in Scheme 1. The main ^{1}H-, ^{13}C-, and ^{119}Sn-NMR characteristics of these mixtures are summarized in Tables 1 and 2.

Under the same reaction conditions, the addition of (−)-menthyldimethyltin hydride (**1**) to (*Z*)-2,3-diphenylpropanenitrile (**4**) gives a mixture of only two diastereoisomers, **9** + **9**′ (Scheme 1), as shown by the ^{1}H-, ^{13}C-, and ^{119}Sn-NMR spectra of the reaction crude product. Again, all attempts to separate the diastereoisomeric mixture were unsuccessful.

The ^{13}C-NMR chemical shifts (Table 1) were assigned through the analysis of the multiplicity of the signals by means of DEPT experiments and taking into account the magnitude of $^{n}J(^{13}C,^{119}Sn)$ coupling constants. As it was found in previous investigations of our group [3, 4b], the use of the Karplus-type relationship existing between the value of the $^{3}J(^{13}C,^{119}Sn)$ coupling constants and the dihedral angle [4], together with ^{1}H-NMR data (Table 2), enabled us to deduce the stereochemistry of the adduct components of each mixture. Thus, the ^{3}J(Sn,C=O) coupling constants (Table 1, C-1) that are not observed in the case of the two adducts components of the mixture **6** + **6**′ and the value of 6.23 Hz for both adducts in the mixture **8** + **8**′ correspond to dihedral angles close to 60° [4b]. Similarly, the values of ^{3}J(Sn–C–C–Ph) coupling constants of ca. 50 Hz for the mixtures **6** + **6**′ and **8** + **8**′ (Table 1, C-2′) indicate a dihedral angle of about 180° between the trialkylstannyl moiety and the phenyl group attached to C-2. In the case of the mixture of adducts **9** + **9**′, the value of 12.3 Hz observed for the ^{3}J(Sn, CN) coupling constants (Table 1, C-1) suggest an angle of around 60°, whereas the values of ca. 30 Hz observed for the ^{3}J(Sn–C–C–Ph) coupling constants (Table 1, C-2′) could be ascribed to a dihedral angle of 180°.

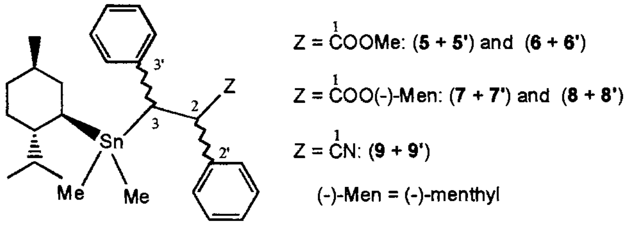
^{1}H-NMR spectra (Table 2) of the mixtures of compounds **6** + **6**′, **8** + **8**′, and **9** + **9**′ show that the ^{3}J(H,H) coupling constants for the protons attached to C-2 and C-3 lie between 9.8 and 12.8 Hz, thus indicating that these protons are antiperiplanar. The ^{3}J(Sn–C–C–H) coupling constants for the mixtures **6** + **6**′, **8** + **8**′, and **9** + **9**′ with values ranging from 36.0 to 52.4 Hz suggest a dihedral angle close to 60°.

Taking into account the previous discussion, it is possible to attribute a *threo* configuration, i.e. (2*R*,3*R*)- and (2*S*,3*S*)-, to the components of the mixtures of diastereoisomers **6** + **6**′, **8** + **8**′, and **9** + **9**′ as shown in Fig. 1(**I**).



Scheme 1. Addition of (−)-menthyldimethyltin hydride (**1**) to alkyl (*E*)-2,3-diphenylpropenoates **2** and **3** and to (*Z*)-2,3-diphenylpropenenitrile (**4**).

Table 1
^{13}C- and ^{119}Sn-NMR data of the mixtures (**5**+**5′**)–(**9**+**9′**)[a]



Mixture no.	Me–Sn [^1J(Sn,C)]	C(1) [^3J(Sn,C)]	C(2) [^2J(Sn,C)]	C(3) [^1J(Sn,C)]	C(2′) [^3J(Sn,C)]	C(3′) [^2J(Sn,C)]	Other signals	^{119}Sn
5+**5′**	−10.04 (278.0)	174.32	54.80	40.53	137.67	144.31	[b]	1.7
	−10.56 (291.6)	(72.9)	(n.o.)	(283.0)	(6.8)	(22.2)		−1.1
	−11.07 (281.4)	174.20	54.61	38.0	137.59	144.28		
	−11.33 (295.0)	(72.0)	(n.o.)	(283.0)	(6.8)	(21.0)		
6+**6′**	−9.83 (272.9)	174.62	54.24	37.03	139.42	143.44	[c]	4.9
	−10.61 (291.6)	(n.o.)	(6.8)	(276.3)	(50.9)	(27.1)		
	−10.6 (289.9)	174.55	54.06		139.36	143.30		
	−10.91 (275.5)	(n.o.)	(5.9)		(51.2)	(27.1)		
7+**7′**	−9.99 (277.4)	173.47	55.20	40.11	138.86	144.40	[d]	−2.82
	−10.64 (278.2)	(72.4)	(n.o.)	(281.8)	(7.2)	(26.9)		
	−11.22 (280.0)	173.33	54.94	38.66	138.69	144.32		
	−11.34 (294.4)	(75.4)	(n.o.)	(287.2)	(7.2)	(26.9)		
8+**8′**	−9.74 (272.8)	174.14	54.80	38.08	140.09	143.90	[e]	3.96
	−10.36 (292.6)	(6.3)	(7.2)	(281.8)	(50.3)	(27.8)		6.62
	−10.96 (290.8)	173.99	54.28	36.50	139.98	143.86		
	−11.09 (274.6)	(6.3)	(7.2)	(280.9)	(51.1)	(27.8)		
9+**9′**	−9.05 (281.8)	121.59	41.17	39.72	136.51	142.23		
	−10.75 (281.8)	(12.3)	(n.o.)	(248.6)	(28.7)	(22.4)		
	−10.27 (299.8)	121.61	41.12	39.65	136.55	141.94		
	−10.61 (299.8)	(12.3)	(n.o.)	(248.5)	(32.3)	(22.4)	[f]	0.50

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to TMS (^{13}C spectra) and Me_4Sn (^{119}Sn spectra); ^nJ(Sn,C), coupling constants in Hz (in brackets); n.o., not observed.

[b] 15.41; 15.57; 21.82; 21.87; 22.32 (5.1); 26.23 (66.1); 26.26 (66.1); 33.56; 33.86; 34.67 (66.9); 35.04 (6.8); 35.07 (6.8); 39.91 (18.6); 40.70 (20.3); 45.75 (16.0); 45.87 (16.1); 51.48; 124.17; 124.30; 126.49 (20.3); 126.62 (21.2); 127.80; 127.87; 128.26 (9.3); 128.53; 128.56; 128.70.

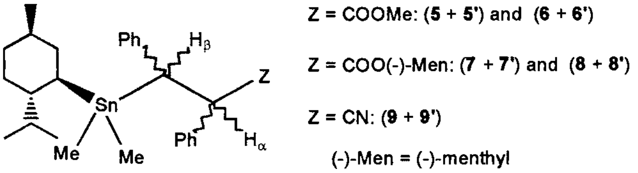
[c] 15.58; 15.62; 21.92; 22.44 (5.1); 22.49 (5.1); 26.40 (65.3); 26.43 (65.3); 33.40 (19.5); 33.70 (19.5); 34.11; 34.47; 35.00 (67.8); 35.07 (67.8); 35.29; 40.46 (20.3); 40.66 (20.3); 45.95 (15.3); 46.00 (15.3); 51.97; 123.59 (11.9); 123.73 (11.9); 126.64; 127.16 (22.0); 127.89; 127.97; 128.00.

[d] 15.56; 15.58; 20.58; 20.64; 21.76; 21.92; 26.36; 26.46; 33.75; 34.04; 34.98; 35.36; 39.68; 40.62; 46.03; 46.64; 127.67; 127.84; 127.97; 128.12; 128.16; 128.18; 128.46; 128.49; 128.53.

[e] 15.37; 15.72; 20.37; 20.82; 21.82; 21.96; 24.96; 25.62; 33.60; 34.13; 35.01; 35.27; 40.43; 40.85; 45.84; 126.47; 127.07; 127.16; 127.76; 127.86; 127.92; 127.95.

[f] 15.48; 21.81; 22.38; 26.27 (66.4); 33.51 (19.8); 34.06 (400.3); 34.82 (67.3); 35.06 (7.2); 40.34 (19.8); 46.07 (16.2); 124.91 (4.5); 127.20; 127.24; 127.28; 127.56; 127.62. 15.54; 21.83; 22.32; 26.22 (66.4); 33.70 (19.7); 34.5 (401.2); 34.46 (68.0); 35.10 (7.1); 40.48 (19.7); 45.99 (16.2); 124.87 (5.4); 128.37; 128.46; 128.50; 128.76; 128.87.

Table 2
^{1}H-NMR data of the mixtures (**5**+**5′**)–(**9**+**9′**)[a]



Mixtures no.	CH_3–Sn ^{3}J(Sn,H)	H_α,^{3}J(H,H) ^{3}J(Sn,H)	H_β, ^{3}J(H,H) ^{2}J(Sn,H)	Other signals
5+5′	−0.45 (45.7)	4.27 (d, 13.1)	3.34 (d, 12.1)	0.54 [d, ^{3}J(H,H) 7.5]; 0.56 [d, ^{3}J(H,H) 7.2];
	−0.34 (46.2)	(41.2)	(50,3)	0.73 [d, ^{3}J(H,H) 7.5]; 3.41 (s); 7.04–7.55 (m)
	−0.27 (46.0)	4.31 (d, 13.2)	3.64 (d, 12.2)	
	−0.10 (45.9)	(41.2)	(51.2)	
6+6′	−0.22 (46.0)	4.33 (d, 12.9)	3.35 (d, 12.4)	0.79 [d, ^{3}J(H,H) 7.5]; 0.83 [d, ^{3}J(H,H) 7.0];
	−0.19 (46,0)	(51.0)	(52.0)	0.90 [d, ^{3}J(H,H) 7.0]; 3.69 (s); 6.89–7.34 (m)
	0.13 (46.0)	4.35 (d, 12,5)	3.43 (d, 12.9)	
	0.14 (46.0)	(52.4)	(52.4)	
7+7′	−0.39 (43.6)	4.09 (d. 14.0)	3.45 (d, 13.4)	0.53 [d, ^{3}J(H,H) 6.7]; 0.75 [d, ^{3}J(H,H) 7.3];
	−0.28 (46.4)	(n.o.)	(n.o.)	0.90 [d, ^{3}J(H,H) 7.1]; 4.53 (m); 6.80–7.23 (m)
	0.08 (46.3)	4.12 (d, 14.0)	3.48 (d, 14.0)	
		(n.o.)	(n.o.)	
8+8′	−0.40 (46.5)	4.22 (d, 12.8)	3.39 (d, 12.8)	0.52 [d, ^{3}J(H,H) 6.8]; 0.78 [d, ^{3}J(H,H) 7.0];
	−0.27 (46.0)	(42.0)	(52.7)	0.84 [d, ^{3}J(H,H) 6.8]; 4.64 (m); 6.83–7.11 (m)
	0.07 (46.4)	4.23 (d, 12.2)	3.20 (d, 12.2)	
		(41.9)	(53.7)	
9+9′	−0.14 (47.6)	4.27 (d, 10.4)	2.93 (d, 10.4)	0.67 [d, ^{3}J(H,H) 6,7]; 0.78 [d, ^{3}J(H,H) 6.7];
	−0.11 (47.0)	(36.6)	(68.4)	0.81 [d, ^{3}J(H,H) 7,3]; 0.85 [d, ^{3}J(H,H) 6.7];
	0.28 (47.0)	4.32 (d, 9.8)	3.01 (d, 9.8)	0.89 [d, ^{3}J(H,H) 7.3]; 0.94 [d, ^{3}J(H,H) 7.1];
	0.29 (47.6)	(36.0)	(67.7)	1.18 (m); 1.47 (m); 1.35 (m); 6.80–7.21 (m)

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to TMS; ^{n}J(Sn,H) and ^{3}J(H,H), coupling constants in Hz (in brackets); multiplicity (in brackets): d, doublet; m, multiplet; n.o., not observed.

The analysis of the ^{13}C-NMR spectra (Table 1) of the mixtures of esters obtained in lower proportion **5** + **5′** and **7** + **7′**, show that the values of the ^{3}J(Sn,C=O) coupling constants lie around 72 Hz which points to a dihedral angle of about 180°. The small values of ^{3}J(Sn–C–C–Ph) coupling constants for these compounds, 6.8 and 7.2 Hz, suggest a dihedral angle close to 60° between the trialkylstannyl group and the phenyl group attached to C-2. ^{1}H-NMR spectra (Table 2) of the mixtures **5** + **5′** and **7** + **7′** show that the ^{3}J(H,H) coupling constants for the protons attached to C-2 and C-3 are within the range 12.1–14.0 Hz, which indicates a dihedral angle of 180° between these protons. These values strongly suggest that the diastereoisomers components of the **5** + **5′** and **7** + **7′** have the *erythro* configuration, i.e. (2*S*,3*R*)- and (2*R*,3*S*)-, as shown in Fig. 1(**II**).

As can be seen in Scheme 1, the main products obtained in the hydrostannation with (−)-menthyldimethyltin hydride of methyl (**2**) and (−)-menthyl (**3**) (*E*)-2,3-diphenyl propenoates as well as the products of the addition of the same hydride to (*Z*)-2,3-diphenylpropenenitrile (**4**) have the *threo* stereochemistry. This clearly indicates that whereas the addition to esters **2** and **3** follows a preferential *syn* steric course, the addition to the unsaturated nitrile **4** takes place following an *anti* steric course.

The stereocontrol observed in radical reactions has frequently been explained in terms of the existence of A-strain effects [5,6]. The A-strain model postulates that a conjugating substituent on the radical-bearing carbon dictates that the smallest substituent on the adjacent stereocenter points to the same direction as the conjugating group. It has also been demonstrated that

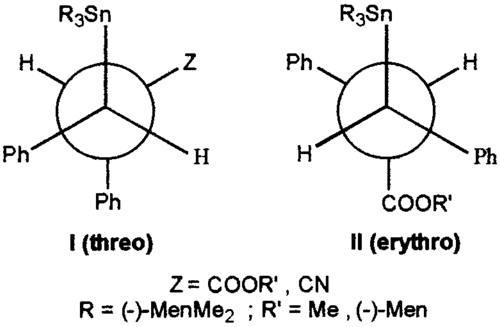


Fig. 1. Preferred conformations of *threo* and *erythro* compounds (only one stereoisomer of each is shown).

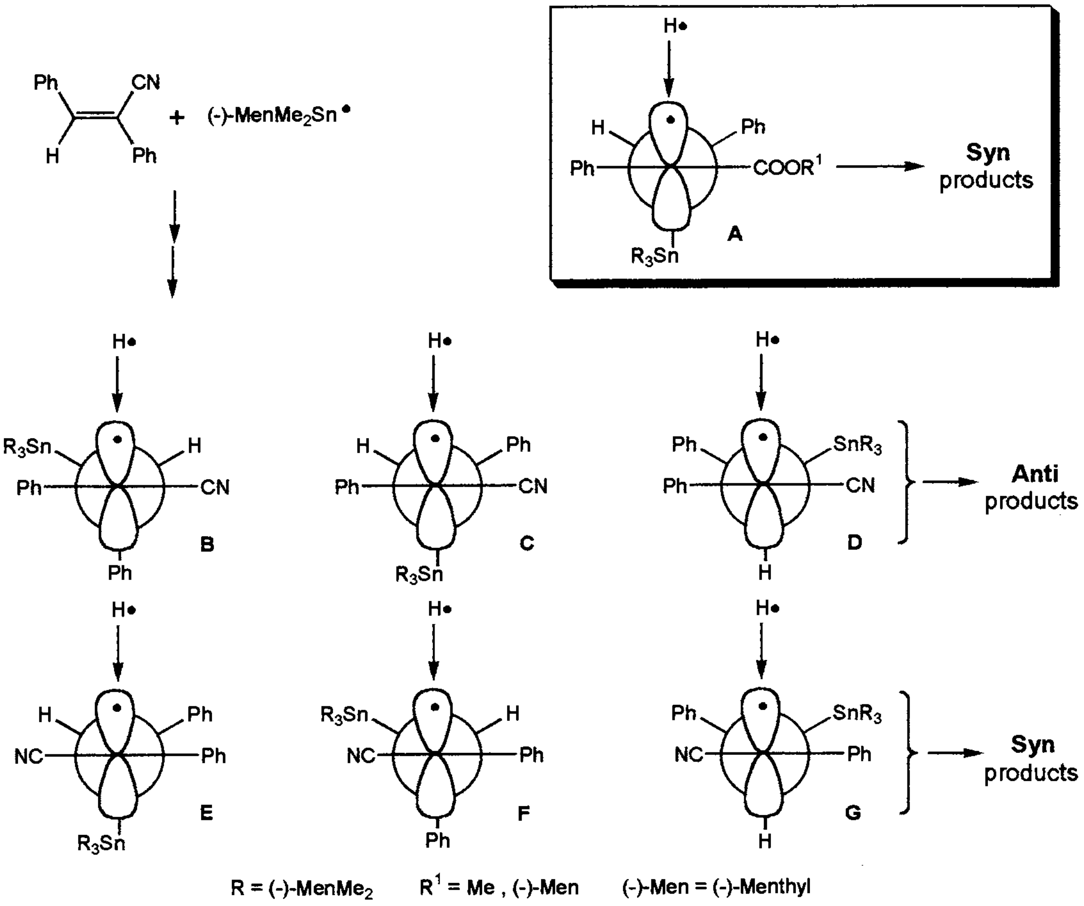


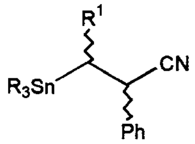
Fig. 2. Intermediate α-phenyl-β-trialkylstannyl radicals (only one enantiomer of each shown).

the preferred conformations for alkyl radicals containing a β-trialkyltin substituent are those in which the trialkylstannyl moiety is eclipsed with the half-filled carbon p orbital due to the gain in stabilization by hyper- and homoconjugative effects which can be as large as 5 kcal mol^{-1} [7]. In the case of the addition of organotin hydrides to alkyl α-phenyl propenoates [3] there are two conjugating substituents attached to the resulting radical carbon: the phenyl group (benzylic system) and the ester group (heteroallylic system). The fact that the phenyl group is a better conjugating group than the ester group [8] together with A-strain effects were the main arguments in favor of type **A** radicals (Fig. 2) as the more stable intermediates in the hydrostannation of alkyl (*E*)-2-phenyl-3-alkyl (phenyl) propenoates [3].

In Fig. 2 are also shown the six possible intermediate alkyl radicals resulting from the addition of (—)-menthyldimethylstannyl radical to (*Z*)-2,3-diphenylpropenenitrile (**4**) as well as the expected products according to the side that occurs the hydrogen transfer by another molecule of tin hydride in the last step of the radical chain. Taking into account that these additions lead only to *threo* products, radicals **B**–**D** will be first considered. Radicals **B** and **D** can be discarded considering that the energetically favored arrangement for the operation of the A-strain model, i.e. the hydrogen atom attached to C-3 pointing to the same direction as the phenyl (conjugating) group attached to the radical carbon is not present in these conformations. Besides, the fact that the tin hydride would be approaching radical **D** between the two largest groups in order to effect the hydrogen transfer makes this radical a possible intermediate only in high-energy pathways and therefore can be discarded.

In radical **C** the conjugating phenyl group points to the same direction as the hydrogen atom attached to C-3 and the trialkylstannyl group occupies an eclipsed position relative to the half-filled carbon p orbital, i.e. the best situation in order to control the stereochemistry of the addition [3]. The analysis of the features of radicals **E** and **F** which would lead to *syn* (*erythro*) products shows that, whereas in radical **E** the trialkylstannyl substituent is eclipsed with the half-filled carbon p orbital and the conjugating phenyl group does not point to the same direction as the hydrogen atom in the neighbouring carbon atom, in radical **F** the conjugating substituent is on the same side as the hydrogen but there is no eclipsing between the trialkylstannyl group and the radical p orbital.

Table 3
Diastereoisomers obtained in the addition of organotin hydrides to (*Z*)-2,3-disubstituted propenenitriles[a,b]



R^1 = Me , Ph
R = Me , n-Bu , Ph , (-)-MenMe$_2$
(-)-Men = (-)-menthyl

Hydride	Configuration	$R^1 = Ph$	$R^1 = Me$
Me_3SnH*	*Threo*	93	100
	Erythro	7	
n-Bu_3SnH	*Treo*	100	100
Ph_3SnH	*Treo*	100	100
(−)-$MenMe_2SnH$	*Treo*	100	–

[a] From the NMR spectra.
[b] See [1a, 9].

From the previous discussion it can be concluded that in the case of the β-triorganoestannyl alkyl radicals any of the effects, i.e. the A-strain effects and the gain in stability due to the eclipsing of the organotin substituent with the radical orbital on the neighbour carbon, cannot dictate the stereochemistry of the radical addition by itself. Therefore, the observed stereoselectivity must be connected with the existence of preferred conformations in the intermediate radicals arising from both factors together.

This conclusion is also supported by previous studies on the hydrostannation of (*Z*)-2,3-disubstituted propenenitriles with a phenyl substituent attached to carbon 2 [1a, 9] where the major or only products were those with the *threo* configuration (Table 3).

These results, together with those reported earlier [1–3], indicate that it would be possible to predict the stereochemistry of the hydrostannation products by considering the type of substituents attached to the olefinic double bond and the preferred conformation of the intermediate radicals resulting from the addition of the organotin radical. Thus, when there is just one conjugating group attached to the carbon radical the preferred conformation should be **A** (Fig. 3), i.e. the conjugating group on the same side as the smaller group in the neighbouring stereocenter and the organotin moiety eclipsed with the half-filled carbon p orbital. When the conjugating groups attached to the carbon radical are two, the preferred conformation should be **B** (Fig. 3), i.e. the best conjugating group [8] will be on the same side as the smaller group in the adjacent carbon and the organotin substituent eclipsed with the carbon p radical.

These studies also show that it is possible to achieve the asymmetric hydrostannation of olefinic systems with achiral and chiral substituents using organotin hydrides with chiral ligands and that the enantioselectivities obtained are very similar to those reached in the additions of achiral organotin hydrides to chiral olefinic systems.

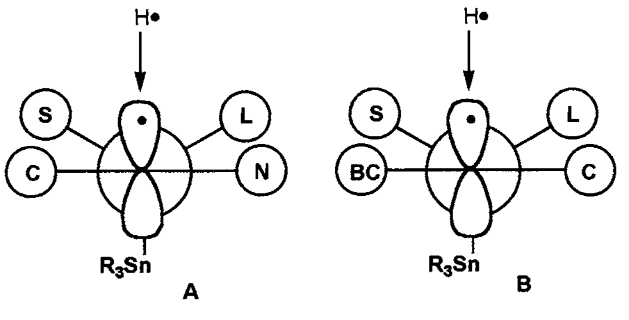


Fig. 3. Preferred conformations of the intermediate alkyl radicals for the hydrogen transfer.

3. Experimental

The NMR spectra were determined partly at Dortmund University (Germany) (^{1}H, ^{13}C and ^{119}Sn), using a Bruker AM 300 instrument), and partly at IQUIOS (Rosario, Argentina) (^{1}H and ^{13}C) with a Bruker AC 200 instrument. Infrared spectra were recorded with a Perkin–Elmer 599B spectrophotometer. All the solvents and reagents used were analytical reagent grade. (−)-Menthyldimethyltin hydride (**1**) [10] and the starting olefins, **2**–**4** [2,11] were prepared as described.

All the reactions were carried out following the same procedure. One experiment is described in detail in order to illustrate the method used.

3.1. Addition of (−)-menthyldimethyltin hydride (1) to methyl (E)-2,3-diphenylpropenoate (2). Synthesis of the mixtures of methyl (2R,3S)- and (2S,3R)-2,3-diphenyl-3-(triphenylstannyl)propanoates (5 + 5′), and methyl (2R,3R)- and (2R,3R)-2,3-diphenyl-3-(triphenylstannyl propanoate) (6 + 6′).

^{1}H-, ^{13}C-, and ^{119}Sn-NMR data of the mixtures of organotin compounds are included in Tables 1 and 2.

Ester **2** (2.43 g, 0.01 mol) was treated for 48 h with tin hydride **1** (6.37 g, 0.022 mol) under nitrogen at 85°C and with azobisisobutyronitrile (AIBN) as a catalyst (this optimal time of reaction and the use of an adequate excess of organotin hydride were indicated by earlier experiments in which the reaction was monitored by taking samples at intervals and observing the disappearance of the Sn–H absorption by IR, and by checking at the end of the reaction that the ^{1}H-NMR spectrum of the reaction mixture no longer showed the presence of unchanged olefin). The ^{1}H-NMR spectrum showed that under these conditions a quantitative yield (based on starting olefin) of a mixture of diastereoisomeric adducts was obtained. The ^{119}Sn-NMR spectrum of the crude product showed three peaks: a big one (91.5%) and two very small (3.2 and 5.3%).

The crude product was purified by column chromatography on silica gel 60. With 98.5:1.5 light petroleum (b.p. 30–65°C)–diethyl ether two fractions were eluted; the main fraction consisted of a mixture of diastereoisomers **6** + **6′** (4.89 g, 0.0093 mol) and the minor fraction was a mixture of diastereoisomers **5** + **5′** (0.39 g, 0.007 mol). We were not able to separate these mixtures either by changing the elution solvents or by vacuum distillation (decomposition).

Under the same reaction conditions, the hydrostannation of ester **3** required 80 h, and the mixtures **8** + **8′** (main fraction) and **7** + **7′** (minor fraction) were eluted with light petroleum (b.p. 30–65°C)/ethyl acetate 97:3.

Under the same reaction conditions, the hydrostannation of nitrile **4** required 15 h, and the mixture **9** + **9′** was eluted with light petroleum (b.p. 30–65°C) + diethyl ether 97:3.

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