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Journal of Organometallic Chemistry 650 (2002) 173–180

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Stereoselective hydrostannation of substituted alkynes with trineophyltin hydride

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Received 2 August 2001; accepted 9 January 2002

Abstract

Hydrostannation of mono- and disubstituted alkynes with trineophyltin hydride (**1**) leads to vinylstannanes in good to excellent yields, the configuration of the products depending on the reaction conditions. Thus, whereas hydrostannation under radical conditions leads stereoselectively to only one of the two possible products corresponding to an *anti* addition in 60–99% yield, the additions catalyzed by bis(triphenylphosphine)palladium dichloride gave mixtures of the *syn* adducts (60–79% yield). Full ^{1}H-, ^{13}C-, and ^{119}Sn-NMR as well as mass spectra data of the organotin adducts are given. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrostannation; Vinylstannanes; Radical; Palladium catalysis; Stereoselectivity

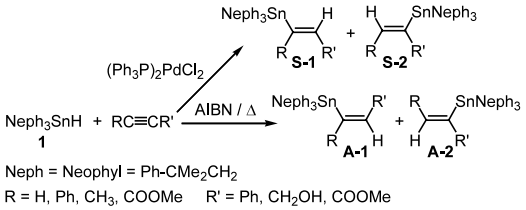
1. Introduction

Vinylstannanes are very useful intermediates in organic synthesis, especially when they have a well defined stereochemistry [1]. Among other important applications, they are used as vinyl anion equivalents, as precursors of vinyllithiums, and in cross-coupling reactions (the Stille reaction). Hydrostannation of alkynes is still the more simple and economical method for the preparation of vinylstannanes. However, in recent publications it has been stated that the main problems of radical hydrostannation are the low yields [2a,2] and that the regio- and stereoselectivities are low [2b,2c]. It has also been stated that, depending on the structure of the alkynes, regio- and stereoselectivities could not be predicted under radical conditions [2c].

We are interested in the synthesis of organotin hydrides with bulky organic ligands and in their chemical properties, especially with regard to the effect of the volume of these ligands on the stereochemistry of reductions and additions [3]. In this paper, we report the results obtained in the addition of trineophyltin hydride (**1**) [3a] to mono- and disubstituted alkynes under radical and palladium catalyzed conditions.

2. Results and discussion

According to previous reports on the addition of organotin hydrides to acetylenes, we expected that whereas the hydrostannation under radical conditions would lead to a mixture of mainly the two regioisomers resulting from an *anti* attack (**A-1** and **A-2**), the palladium catalyzed reactions would yield mainly two regioisomers corresponding to a *syn* addition (**S-1** and **S-2**), as shown in Scheme 1.



Scheme 1. Possible adducts resulting from the hydrostannation of substituted alkynes with trineophyltin hydride (**1**).

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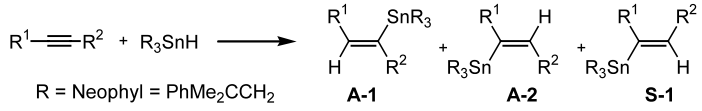
PII: S0022-328X(02)01213-5

We first carried out the addition of trineophyltin hydride (**1**) under free radical conditions: nitrogen atmosphere, 0.01 equivalents of azobisisobutyronitrile (AIBN), without solvent at 90 °C (Section 3.1.1) or in toluene at the same temperature (Section 3.1.2), and UV irradiation in toluene (Section 3.1.3) to a series of eight substituted alkynes. The results obtained are summarized in Table 1.

This table shows that, according to the reaction conditions, the addition of **1** to propargyl alcohol, methyl propiolate, diphenylethyne, 3-phenyl-2-propyn-1-ol, 2-butyn-1-ol, and methyl 3-phenylpropiolate leads almost exclusively to the *Z*-vinylstannanes resulting from an *anti* attack. In Table 1, it could also be seen that in the additions to phenylethyne and dimethyl acetylenedicarboxylate under the three radical conditions studied, and methyl propiolate under appropriate conditions, *E*-adducts were de soles products. The formation of the *E*-adducts **2**, **5** and **11**, could be explained taking into account that the known isomerization of the initially formed kinetic *Z*-products by further addition/elimination of the stannyl radical would lead to the thermodynamically more stable *E*-vinylstannanes [2c,4].

The geometry assigned to compounds **3**, **4**, and **6**–**10** follows from the large ^{3}J(Sn,H) coupling constants, mostly well over 110 Hz, that indicate the existence of *trans* H–C–C–Sn linkages in these compounds. The observed ^{3}J(Sn,H) coupling constants for compounds **2**, **5** and **11** —between 23 and 75 Hz (Table 2)—clearly indicate the existence of a *cis* H–C–C–Sn linkage in these compounds. These structures were confirmed by other ^{1}H- and ^{13}C-NMR data.

Table 1
Trienophyltin hydride radical addition to substituted alkynes



Compound number	Method [a]	Time (h)	R^1	R^2	**A-1** (%)	**A-2** (%)	**S-1** (%)	Yield [b] (%)	^{119}Sn [c] (ppm)
2	A	1	H	Ph			100 [d]	99	−93.7
2	B	5	H	Ph			100 [d]	99	
2	C	0.5	H	Ph			100 [d]	100	
3	A	6	H	CH_2OH		100		69	−97.5
3	B	10	H	CH_2OH		100		55	
3	C	26	H	CH_2OH		100		49	
4 and **5**	A	1	H	COOMe		34 (**4**)	66 [e] (**5**)	87	**4**: −92.4
									5: −83.5
4 and **5**	B	1	H	COOMe		91 (**4**)	9 [e] (**5**)	65	
5	C	0.75	H	COOMe			100 [e]	100	
6	A	5	Ph	Ph		100		70	−89.0
6	B	14	Ph	Ph		100		41	
6	C	72	Ph	Ph					[f]
7	A	5	CH_2OH	Ph		100		61	−88.8
7	B	6	CH_2OH	Ph		100		75	
7	C	10	CH_2OH	Ph		100		22	
8 and **9**	A	9	CH_2OH	Me	12 (**8**)	88 (**9**)		60	**8**: −93.2
									9: −94.4
9	B	24	CH_2OH	Me		100		55	
9	C	19	CH_2OH	Me					[f]
10	A	2	Ph	COOMe		100		80	−81.7
10	B	2	Ph	COOMe		100		68	
10	C	1	Ph	COOMe		100		100	
11	A	2	COOMe	COOMe			100	80	−80.7
11	B	3	COOMe	COOMe			100	88	
11	C	1	COOMe	COOMe			100	100	

[a] The reaction were carried out under a nitrogen atmosphere; ratio hydride/alkyne = 1. Method A, AIBN 0.01 equivalents, heating at 90 °C without solvent. Method B, AIBN 0.01 equivalents, heating at 90 °C in Toluene. Method C, UV irradiation in toluene.

[b] Yields of products isolated from the column chromatography.

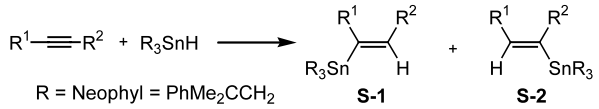
[c] In $CDCl_3$; in ppm with respect to Me_4Sn.

[d] The product isolated was (*E*)-1-trineophylstannyl-2-phenylethylene (2), see text.

[e] See text.

[f] No adduct formation observed.

Table 2
Trineophyltin hydride palladium-catalized additions to substituted alkynes [a]



Compound no.	R^1	R^2	**S-1** (%) [b]	**S-2** (%) [b]	Yield [c] (%)	^{119}Sn [d] (ppm)
12	Ph	H	100		99	−79.8
13 and **14**	H	CH_2OH	30 (**13**)	70 (**14**)	67	**13:** −84.7 **14:** −85.6
15	Ph	Ph	100		79	−72.3
16 and **17**	CH_2OH	Ph	67 (**16**)	33 (**17**)	60	**16:** −77.2 **17:** −77.6
18 and **19**	CH_2OH	Me	53 (**18**)	47 (**19**)	70	**18:** −82.5 **19:** −76.4
5 and **20**	H	COOMe	31 (**5**)	69 (**20**)	82	**9:** −83.5 **20:** −76.8
21 and **22**	Ph	COOMe	33 (**21**)	67 (**22**)	70	**21:** −55.6 **22:** −68.1
11	COOMe	COOMe	100		94	−80.7

[a] The reaction were carried out under a nitrogen atmosphere in THF; ratio hydride/alkyne = 1; $PdCl_2(Ph_3P)_2$: 2%; reaction time: 30 min.
[b] By integration of the ^{119}Sn-NMR spectrum.
[c] Yields of products isolated from the column chromatography.
[d] In $CDCl_3$.

The addition of trineophyltin hydride (**1**) to the same eight alkynes at r.t. in THF containing 2% of bis(triphenylphosphine)palladium(II) chloride led, after 30 min of reaction, in most cases to mixtures of adducts. The results obtained are summarized in Table 2. This Table shows that all the regioisomers formed are those resulting from a *syn* attack (Scheme 1, **S-1** and **S-2**).

The stereochemistry of compounds **11**–**22** was assigned taking into account that the observed ^3J(Sn,H) coupling constants were in the range 65–85 Hz, clearly indicating a *cis* arrangement of the proton attached to vinyl carbon 2 and the trineophyltin moiety attached to vinyl carbon 1 of these adducts. Other ^{1}H- and ^{13}C-NMR data confirmed also the assigned structures (Tables 3 and 4).

These results clearly demonstrate that, contrary to what has previously been stated [2a,2b,2c], it is possible using organotin hydrides with bulky organic ligands such as **1** to carry out radical hydrostannation of mono- and disubstituted alkynes with very good to excellent stereoselectivities. The *anti*-addition products were mainly obtained in satisfactory to excellent yields (55–100%), and in only one case a mixture of the two possible regioisomers in a ratio 9/8 = 7.33 was observed.

It should be noted that in a recent publication it has been reported that the radical addition of tri-*n*-butyltin hydride to the 3-phenyl-2-propyne-1-ol leads to a mixture of (*E*)- and (*Z*)-3-phenyl-2-propen-1-ol (ratio *E*/*Z* = 61:39) in 72% yield [5].

On the other hand, the addition of **1** catalyzed by bis(triphenylphosphine) palladium(II) chloride to the same alkynes, also takes place stereoselectively but leads in all cases to the products of a *syn* attack, mainly as a mixture of the two possible regioisomers in good to excellent yields (60–99%).

The chemical reactivity of the new vinyltrineophylstannanes is similar to that of other vinyltriorganostannanes. Thus, the iododestannylation of (*E*)-1-trineophylstannyl-2-phenylethene (**2**) leads to (*E*)-β-iodostyrene [6] in 82% yield and the Stille reaction of **2** with bromobenzene gives *trans*-stilbene in 86% yield.

Further investigations in order to study the effect of changes of catalyst, alkyne, and the size of the ligands of the organotin hydrides on the stereochemistry of these additions are in progress.

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) with a Bruker AC 200 instrument. Mass spectra were obtained using a Finnigan MAT Model 8230 at Dortmund University. Irradiations were conducted in a reactor equipped with four 250-W lamps with peak emission at 350 nm (Philips Model HPT) water cooled. All the solvents and reagents used were analytical reagent grade. Trineophyltin hydride (**1**) was prepared as described [7]. Phenylacetylene, diphenylacetylene, propiolic acid, phenylpropiolic acid, acetylenedicarboxylic acid, propargyl alcohol, 2-butyn-1-ol, and bis(triphenylphosphine) palladium(II) chloride

procedures before using. The methyl esters of the acids were obtained following known techniques [8]. Phenylpropargyl alcohol was obtained by reduction of methyl phenylpropiolate with lithiumaluminium hydride [9].

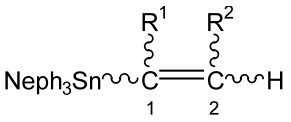
All the reactions were carried out following the same procedure. One experiment is described in detail in order to illustrate the methods used.

3.1. Addition of trineophyltin hydride (*1*) to substituted alkynes under radical conditions

3.1.1. Method A

Methyl propiolate (0.15 g, 1.78 mmol) was treated for 1 h with hydride **1** (0.924 g, 1.78 mmol) under nitrogen at 90 °C and with AIBN as a catalyst (this

Table 3
^{13}C-NMR data of vinyltin adducts **2**–**22** [a]



Compound no.	R^1	R^2	C(1)	C(2)	R^1 [b]	R^2 [b]	*
2	H	Ph	134.89 (447.0)	145.24 (35.0)		140.95 (10.7)	c
3	H	CH_2OH	134.09 (366.0)	144.63 (25.2)		65.41 (37.9)	d
4	H	COOMe	158.26 (320.7)	133.48 (13.7)		167.88 (13.7)	e
5	H	COOMe	159.94 (315.7)	133.25 (15.6)		164.0 (35.4)	f
6	Ph	Ph	151.89 (311.7)	143.77 (20.4)	140.11 (19.4)	149.09 (29.1)	g
7	CH_2OH	Ph	148.32 (332.7)	138.74 (16.2)	69.55 (52.5)	140.20 (22.3)	h
8	Me	CH_2OH	144.73 (367.6)	139.14 (26.3)	20.6 (46.5)	64.68 (37.0)	i
9	CH_2OH	Me	144.95 (371.0)	136.11 (24.3)	70.18 (48.6)	20.65 (36.9)	j
10	COOMe	Ph	141.01 (314.8)	152.84 (21.2)	172.26 (12.7)	138.47 (16.3)	k
11	COOMe	COOMe	161.88 (416.9)	128.28 (16.5)	172.69 (no)	163.58 (no)	l
12	Ph	H	150.87 (375.1)	128.07 (11.7)	151.29 (11.7)		m
13	H	CH_2OH	130.29 (425.4)	144.39 (24.2)		66.04 (68.0)	n
14	CH_2OH	H	155.53 (336.3)	122.53 (21.4)	68.49 (58.3)		o
15	COOMe	H	139.25 (24.0)	148.29 (324.0)	171.61 (14.3)		u
16	Ph	Ph	145.49 (320.6)	138.91 (31.1)	152.16 (35.2)	137.64 (60.2)	p
17	CH_2OH	Ph	150.62 (346.3)	140.46 (24.1)	143.86 (26.9)	60.69 (52.5)	q
18	Ph	CH_2OH	137.89 (nd)	(138.46 (27.2)	63.80 (29.2)	152.49 (19.5)	r
19	Me	CH_2OH	143.45 (381.0)	139.28 (27.2)	18.62 (42.8)	59.04 (62.2)	s
20	CH_2OH	Me	146.70 (410.1)	135.63 (25.3)	62.40 (31.1)	14.99 (58.3)	t
21	Ph	COOMe	141.85 (256.3)	141.18 (14.2)	137.11 (46.8)	173.71 (38.4)	v
22	COOMe	Ph	164.14 (nd)	124.19 (13.5)	172.71 (17.9)	144.62 (16.3)	w

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to IMS; ^nJ(Sn,C) coupling constants, in Hz On brackets); nd, not determined.
[b] When R^1 and R^2 = pH = chemical shift of the *ipso* carbon.
* Other signals:
[c] 32.07 (335.3); 32.85 (35,0); 38.11 (18.4); 125.35; 125.42; 127.04; 127.84; 127.97; 128.04; 151.69 (27.2).
[d] 32.36 (336.3); 32.98 (35.9); 38.06 (19.4); 125.32; 125.38; 127.92; 151.06 (20.4).
[e] 32.5 (349.8); 32.9 (36.9); 38.0 (19.4); 125.8; 125.9; 143.0; 152.0.
[f] 30.5 (339.2); 32.9 (37.0); 36.9 (19.2); 124.1; 124.6; 132.5; 150.0.
[g] 32.34 (321.0); 32.44 (33.0); 37.82 (18.5); 125.25; 125.35; 125.44; 127.05; 127.26; 127.87; 127.92; 128.10; 128.54; 151.69 (27.2).
[h] 31.94 (344.6); 32.70 (35.0); 37.94 (19.4); 125.34; 125.37; 126.79; 127.88; 128.00; 128.43; 151.38 (24.3).
[i] 32.00 (307.9); 32.93 (36.2); 38.08 (19.2); 125.15; 125.44; 128.30; 151.29.
[j] 31.64 (323.4); 32.80 (35.0); 38.02 (18.5); 125.34; 125.42; 127.87; 151.38 (22.4).
[k] 32.33 (34.0); 33.16 (327.2); 37.86 (18.5); 51.57; 125.24; 125.29; 127.81; 128.00; 128.27; 132.83; 151,58 (32.1).
[l] 31.13 (332.7); 32.9 (42.8); 37.55 (19.2); 51.02; 50.12; 125.12; 125.6; 128.09; 150.04.
[m] 31.23 (330.5); 33.10 (36.9); 38.01 (17.5); 125.20; 125.24; 125.43; 125.44; 125.92; 126.68 (15.6); 128.01; 128.32; 128.41 (27.2); 150.49 (21.4).
[n] 31.18 (340.2); 33.11 (36.9); 38.04 (19.4); 125.36; 125.42; 127.97; 151.27 (19.4).
[o] 30.70 (330.4); 33.22 (38.9); 37.96 (19.4); 125.45; 127.96; 151,04 (17.5).
[p] 31.4 (334.5); 32.9 (36.7); 38.3 (19.0); 125.2; 125.3; 127.8; 151.6.
[q] 30.75 (322.7); 33.21 (38.9); 37.89 (19.4); 125.04; 15.42; 125.46; 126.43; 126.50; 127.80; 128.04; 128.53; 129.04; 151.27 (17.5).
[r] 30.84 (325.8); 33.15 (36.9); 37.85 (18.5); 125.13; 125.29; 126.53 (14.9); 127.90; 127.92; 151.13 (18.5).
[s] 32.07 (314.9); 33.26 (36.9); 38.24 (19.4); 125.50; 125.62; 126.61; 127.99; 128.77; 130.86; 151.38 (19.5).
[t] 30.68 (322.7); 33.27 (36.9); 37.95 (17.5); 125.36; 125.45; 127.96; 151.27 (17.5).
[u] 31.39 (326.6); 33.20 (36.9); 38.10 (19.4); 125.36; 125.55; 127.88; 151.38 (17.5).
[v] 31.36 (340.2); 33.14 (40.5); 37.70 (18.5); 51.09; 125.32; 125.47; 127.48; 127.78; 127.89; 128.03; 128.23; 128.45; 130.56; 132.86; 150.85 (19.2).
[w] 30.56 (333.0); 33.14 (38.3); 37.69 (18.5); 50.78; 125.27; 125.48; 128.03; 128.15; 150.72 (17.7).

optimal time of reaction was 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). The ^{119}Sn-NMR spectrum of the crude product showed that it consisted of a mixture of two compounds: methyl (*Z*)-3-(trineophylstannyl)propenoate (**4**), peak at −92.4 ppm, (34%), and (*E*)-3-(trineophylstannyl)propenoate (**5**), peak at −83.5 ppm, (66%). Flash chromatography (silica gel 60) of the mixture afforded **4** (0.31 g, 0.52 mmol, 29.6%) and **5** (0.62 g, 1.02 mmol, 57.4%), in the fractions eluted with hexane/diethyl ether (97:3).

3.1.2. Method B

To a solution of methyl propiolate (0.15 g, 1.78 mmol) and AIBN (0.0023 g) in dry toluene (15 ml) under nitrogen was added **1** (0.924 g, 1.78 mmol) and the mixture was heated at 90 °C during 1 h. The solvent was distilled off under reduced pressure. The ^{119}Sn-NMR spectrum showed that under these conditions a mixture of two compounds was formed: methyl (*Z*)-3-(trineophylstannyl)propenoate (**4**) (91%) and methyl (*E*)-3-(trineophylstannyl)propenoate (**5**) (9%). Flash chromatography (silica gel 60) of the mixture afforded **4** (0.65 g, 1.08 mmol, 59.2%) and **5** (0.04 g, 0.067 mmol, 5,8%), in the fractions eluted with hexane/diethyl ether (97:3).

3.1.3. Method C

A solution of methyl propiolate (0.15 g, 1.78 mmol) and **1** (0.924 g, 1.78 mmol) in dry toluene (15 ml) under nitrogen was irradiated at room temperature (r.t.) during 45 min. The solvent was distilled off under reduced pressure. The ^{119}Sn-NMR spectrum showed that under these conditions only methyl (*E*)-3-(trineophylstannyl)propenoate (**5**) in quantitative yield was obtained.

Table 4
^{1}H-NMR spectra of compounds **2**–**22**

Number	Chemical shifts (δ, in ppm)
2	0.85 (s, 3H, ^{2}J(Sn,H) 48.7); 0.87 (s, 3H, ^{2}J(Sn,H) 50.7); 1.09 (s, 9H); 1.10 (s, 9H); 5.55 (d, 1H, ^{3}J(H,H) 14.1; ^{2}J(Sn,H) 63.0); 5.56 (d, 1H, ^{3}J(H,H) 14.1; ^{3}J(Sn,H) 64.0); 6.83–7.42 (m, 20H)
3	0.97 (s, 6H, ^{2}J(Sn,H) 49.7); 1.13 (s, 18H); 3.69 (m, 2H); 5.42 (d, 1H, ^{3}J(H,H) 12.8; ^{2}J(Sn,H) 69.1); 6.17 (dt, 1H, ^{3}J(H,H) 6.3; ^{3}J(H,H) 12.8; ^{3}J(Sn,H) 142.1); 7.05–7.25 (m, 15H)
4	1.10 (s, 2H); 1.15 (s, 6H); 3.61 (s, 3H); 6.17 (d, 1H, ^{3}J(H,H) 13.3; ^{2}J(Sn,H) 119.4); 6.24 (d, 1H, ^{3}J(H,H) 13.3; ^{3}J(Sn,H) 169.1); 7.03–7.22 (m, 5H)
5	0.91 (s, 2H); 1.10 (s, 6H); 3.65 (s, 3H); 5.80 (d, 1H, ^{3}J(H,H) 19.3; ^{2}J(Sn,H) 56.7); 5.82 (d, 1H, ^{3}J(H,H) 19.3; ^{3}J(Sn,H) 74.9); 6.83–7.30 (m, 5H)
6	0.88 (s, 6H, ^{2}J(Sn,H) 50.4); 0.98 (s, 18H); 6.97–7.26 (m, 26H)
7	0.99 (s, 6H, ^{2}J(Sn,H) 50.7); 1.03 (s, 18H); 3.87 (bs, 2H, ^{3}J(Sn,H) 26.8); 5.17 (s, 1H, ^{3}J(Sn,H) 177.2); 7.00–7.30 (m, 20H)
8	1.15 (s, 6H, ^{2}J(Sn,H) 48.8); 1.20 (s, 18H); 1.80 (d, 3H, ^{4}J(H,H) 1.1; ^{3}J(Sn,H) 42.3); 3.70 (m, 2H); 5.96 (tq, 1H, ^{4}J(H,H) 1.1, ^{3}J(H,H) 6.7, ^{3}J(Sn,H) 143.3); 6.84–7.36 (m, 15H)
9	1.12 (s, 6H, ^{2}J(Sn,H) 50.4); 1.14 (s, 18H); 1.48 (d, 3H, ^{3}J(H,H) 6.8); 3.85 (bs, 2H, ^{3}J(Sn,H) 38.1); 6.00 (qt, 1H, ^{4}J(H,H) 1.5; ^{3}J(H,H) 6.8; ^{3}J(Sn,H) 127.5); 7.05–7.21 (m, 15H)
10	1.02 (s, 18H); 1.05 (s, 6H, ^{2}J(Sn,H) 49.9); 3.63 (s, 3H); 6.70–7.62 (m, 20H); 8.16 (s, 1H ^{3}J(Sn,H) 107.1)
11	0.95 (s, 2H); 1.08 (s, 6H); 3.65 (s, 3H); 3.75 (s, 3H); 5.58 (s, 1H, ^{3}J(Sn,H) 23.2); 6.95–7.25 (m, 5H)
12	0.93 (s, 3H, ^{2}J(Sn,H) 48.7); 0.95 (s, 3H, ^{2}J(Sn,H) 49.7); 1.14 (s, 9H); 1.16 (s, 9H); 5.20 (d, 1H, ^{2}J(H,H) 2.5, ^{3}J(Sn,H) 65.3); 5.70 (d, 1H, ^{2}J(H,H) 2.5, ^{3}J(Sn,H) 135.5); 6.80–7.28 (m, 20H)
13	0.95 (s, 6H, ^{2}J(Sn,H) 50.7); 1.14 (s, 18H); 3.78 (m, 2H); 5.23 (dt, 1H, ^{4}J(H,H) 1.76, ^{3}J(H,H) 18.8, ^{2}J(Sn,H) 76.0); 5.58 (dt, 1H, ^{3}J(H,H) 4.5, ^{3}J(H,H) 18.8, ^{3}J(Sn,H) 67.7); 6.91–8.38 (m, 15H)
14	0.98 (s, 6H, ^{2}J(Sn,H) 50.2); 1.14 (s, 18H); 3.68 (m, 2H, ^{3}J(Sn,H) 25.1); 5.01 (dt, 1H, ^{4}J(H,H) 1.8, ^{2}J(H,H) 1.8, ^{3}J(Sn,H) 70.2); 5.63 (dt, 1H, ^{4}J(H,H) 2.0, ^{2}J(H,H) 1.8, ^{3}J(Sn,H) 137.5); 6.94–7.26 (m, 15H)
15	1.00 (s, 2H); 1.09 (s, 6H); 3.58 (s, 3H); 5.55 (d, 1H, ^{3}J(H,H) 2.4; ^{2}J(Sn,H) 56.9); 6.52 (d, 1H, ^{3}J(H,H) 2.4; ^{3}J(Sn,H) 26.7); 6.98–7.21 (m, 5H)
16	0.87 (s, 6H, ^{2}J(Sn,H) 48.2); 1.02 (s, 18H); 6.35 (s, 1H, ^{3}J(Sn,H) 69.3); 6.66–7.27 (m, 25H)
17	0.88 (s, 18H); 1.11 (s, 6H, ^{2}J(Sn,H) 64.4); 3.76 (d, 2H, ^{3}J(H,H) 6.1), 5.49 (t, 1H, ^{3}J(H,H) 6.1, ^{3}J(Sn,H) 77.4); 6.57–6.69 (m, 5H); 6.85–7.32 (m, 15H)
18	1.13 (s, 6H, ^{2}J(Sn,H) 54.2); 1.18 (s, 18H); 3.90 (m, 2H, ^{3}J(Sn,H) 42.7); 5.20 (s, 1H); 6.39 (bs, 1H, ^{3}J(Sn,H) 85.3); 7.20–7.54 (m, 20H)
19	0.95 (s, 6H, ^{2}J(Sn,H) 49.2); 1.11 (s, 18H); 1.40 (s, 3H, ^{3}J(Sn,H) 47.7); 3.95 (d, 2H, ^{3}J(H,H) 5.8); 5.33 (t, 1H, ^{3}J(H,H) 5.8, ^{3}J(Sn,H) 85.3); 6.97–7.25 (m, 15H)
20	1.02 (s, 18H); 1.13 (s, 6H, ^{2}J(Sn,H) 40.6); 1.44 (d, 3H, ^{3}J(H,H) 6.5), 3.72 (d, 2H, ^{4}J(H,H) 4.8, ^{3}J(Sn,H) 49.4); 5.34 (m, 1H, ^{3}J(Sn,H) 70.3); 6.93–7.36 (m, 15H)
21	0.99 (s, 6H, ^{2}J(Sn,H) 56.2); 1.11 (s, 18H); 3.62 (s, 3H); 6.27 (s, 1H, ^{3}J(Sn,H) 59.2); 6.63–7.34 (m, 20H)
22	0.84 (s, 6H, ^{2}J(Sn,H) 49.7); 1.36 (s, 18H); 3.46 (s, 3H); 5.84 (s, 1H, ^{3}J(Sn,H) 56.2); 6.63–7.34 (m, 20H)

In $CDCl_3$; multiplicity and *J* values in parentheses; coupling constants in Hz; bs, broad singlet.

3.2. Addition of trineophyltin hydride (**1**) to substituted alkynes catalyzed by bis(triphenylphosphine) palladium(II) chloride

To a solution of methyl propiolate (0.15 g, 1.78 mmol) and bis(triphenylphosphine) palladium(II) chloride (0.025 g, 0.0358 mmol) in dry THF (5 ml) under nitrogen was added **1** (0.924 g, 1.78 mmol), and the mixture was stirred at r.t. during 30 min. The solvent was distilled off under reduced pressure. The ^{119}Sn-NMR spectrum showed that under these conditions a mixture of two compounds was formed: methyl (*E*)-3-(trineophylstannyl)propenoate (**5**) (31%) and methyl 2-(trineophylstannyl)propenoate (**20**) (69%). Flash chromatography (silica gel 60) of the mixture afforded **5** (0.22 g, 0.37 mmol, 26%) and **20** (0.49 g, 0.83 mmol, 56%), in the fractions eluted with hexane/diethyl ether (85:15).

3.2.1. Mass spectra of the new vinyltin compounds

*3.2.1.1. (E)-trineophyltinphenylethylene (**2**).* MS (*m*/*z*, relative intensity): 622 (M^+, Sn-pattern); 519 (4%, $[SnNeof_3]^+$); 489 (100%, $[M - Neof]^+$, Sn-pattern); 464 (8%, Sn-pattern); 431 (4%, Sn-pattern); 423 (2%, Sn-pattern); 385 (1%, $[SnNeof_2]^+$); 375 (5%, Sn-pattern); 355 (2%, $[M - Neof_2]^+$, Sn-pattern); 253 (4%, $[SnNeof]^+$); 223 (10%, $[M - Neof_3]^+$, Sn-pattern); 197 (12%, Sn-pattern); 105 (9%, $[M - SnNeof_3]^+$); 118 (6%, $[Sn]^+$).

*3.2.1.2. (Z)-3-trineophyltin-2-propenol (**3**).* MS (*m*/*z*, relative intensity): 576 (M^+; Sn-pattern); 519 (13%, $[SnNeof_3]^+$); 443 (100%, $[M - Neof]^+$, Sn-pattern); 403 (20%, Sn-pattern); 385 (17%, $[SnNeof_2]^+$); 253 (15%, $[SnNeof]^+$); 197 (30%, Sn-pattern); 177 (5%, $[M - Neof_3]^+$, Sn-pattern); 133 (10%, $[Neof]^+$); 118 (3%, $[Sn]^+$); 57 (3%, $[M - SnNeof_3]^+$).

*3.2.1.3. (Z)-3-trineophyltin-2-propenoic acid methyl ester (**4**).* MS (*m*/*z*, relative intensity): 604 (M^+; Sn-pattern); 519 (10%, $[SnNeof_3]^+$); 471 (100%, $[M - Neof]^+$, Sn-pattern); 385 (3%, $[SnNeof_2]^+$); 338 (4%, $[M - Neof_2]^+$, Sn-pattern); 253 (14%, $[SnNeof]^+$); 205 (9%, $[M - Neof_3]^+$, Sn-pattern); 133 (7%, $[Neof]^+$); 118 (5%, $[Sn]^+$).

*3.2.1.4. (E)-3-trineophyltin-2-propenoic acid methyl ester (**5**).* MS (*m*/*z*, relative intensity): 604 (M^+; Sn-pattern); 519 (11%, $[SnNeof_3]^+$); 471 (100%, $[M - Neof]^+$, Sn-pattern); 385 (5%, $[SnNeof_2]^+$); 338 (3%, $[M - Neof_2]^+$, Sn-pattern); 253 (15%, $[SnNeof]^+$); 205 (10%, $[M - Neof_3]^+$, Sn-pattern); 133 (7%, $[Neof]^+$); 118 (4%, $[Sn]^+$).

*3.2.1.5. (Z)-trineophyltin-1,2-diphenylethylene (**6**).* MS (*m*/*z*, relative intensity): 696 (M^+; Sn-pattern); 565 (100%, $[M - Neof]^+$, Sn-pattern); 519 (35%, $[SnNeof_3]^+$); 431 (2%, $[M - Neof_2]^+$, Sn-pattern); 385 (2%, $[SnNeof_2]^+$); 297 (13%, $[M - Neof_3]^+$, Sn-pattern); 253 (10%, $[SnNeof]^+$); 197 (38%, Sn-pattern); 177 (10%, $[M - SnNeof_3]^+$); 133 (6%, $[Neof]^+$); 118 (5%, $[Sn]^+$).

*3.2.1.6. (Z)-2-trineophyltin-3-phenyl-2-propenol (**7**).* MS (*m*/*z*, relative intensity): 652 (M^+; Sn-pattern); 519 (100%, $[M - Neof]^+$, Sn-pattern); 402 (17%, Sn-pattern); 384 (13%, $[M - Neof_2]^+$, Sn-pattern); 253 (11%, $[M - Neof_3]^+$, Sn-pattern); 197 (19%, Sn-pattern); 133 (10%, $[M - SnNeof_3]^+$); 118 (3%, $[Sn]^+$); 55 (11%, $[C_3H_3O]^+$).

*3.2.1.7. (Z)-3-trineophyltin-2-butenol (**8**).* MS (*m*/*z*, relative intensity): 590 (M^+; Sn-pattern); 519 (6%, $[SnNeof_3]^+$); 457 (100%, $[M - Neof]^+$, Sn-pattern); 443 (14%, Sn-pattern); 385 (11%, $[SnNeof_2]^+$); 324 (3%, $[M - Neof_2]^+$, Sn-pattern); 253 (20%, $[SnNeof]^+$) 197 (25%, Sn-pattern); 191 (10%, $[M - Neof_3]^+$, Sn-pattern); 133 (5%, $[Neof]^+$); 118 (2%, $[Sn]^+$); 105 (10%, $[C_8H_9]^+$); 55 (26%, $[C_3H_3O]^+$).

*3.2.1.8. (Z)-2-trineophyltin-2-butenol (**9**).* MS (*m*/*z*, relative intensity): 590 (M^+; Sn-pattern); 519 (7%, $[SnNeof_3]^+$); 457 (100%, $[M - Neof]^+$, Sn-pattern); 443 (13%, Sn-pattern); 385 (11%, $[SnNeof_2]^+$); 324 (2%, $[M - Neof_2]^+$, Sn-pattern); 253 (15%, $[SnNeof]^+$); 197 (27%, Sn-pattern); 191 (9%, $[M - Neof_3]^+$, Sn-pattern); 133 (6%, $[Neof]^+$); 118 (4%, $[Sn]^+$); 105 (11%, $[C_8H_9]^+$); 55 (31%, $[C_3H_3O]^+$).

*3.2.1.9. (Z)-3-trineophyltin-3-phenyl-2-propenoic acid methyl ester (**10**).* MS (*m*/*z*, relative intensity): 680 (M^+; Sn-pattern); 547 (100%, $[M - Neof]^+$, Sn-pattern); 519 (71%, $[SnNeof_3]^+$); 415 (3%, $[M - Neof_2]^+$, Sn-pattern); 385 (5%, $[SnNeof_2]^+$); 281 (18%, $[M - Neof_3]^+$, Sn-pattern); 253 (10%, $[SnNeof]^+$); 197 (30%, Sn-pattern); 149 (7%, Sn-pattern); 133 (8%, $[Neof]^+$); 118 (3%, $[Sn]^+$); 105 (8%, $[C_8H_9]^+$).

*3.2.1.10. (E)-2-trineophyltin-maleic acid dimethyl ester (**11**).* MS (*m*/*z*, relative intensity): 662 (M^+; Sn-pattern); 529 (100%, $[M - Neof]^+$, Sn-pattern); 519 (40%, $[SnNeof_3]^+$); 396 (4%, $[M - Neof_2]^+$, Sn-pattern); 385 (2%, $[SnNeof_2]^+$); 277 (6%, $[M - SnNeof_2]^+$); 263 (20%, $[M - Neof_3]^+$, Sn-pattern); 197 (20%, Sn-pattern); 143 (20%, $[M - SnNeof_3]^+$); 133 (10%, $[Neof]^+$); 118 (3%, $[Sn]^+$).

*3.2.1.11. 1-Trineophyltin-1-phenylethylene (**12**).* MS (*m*/*z*, relative intensity): 622 (M^+; Sn-pattern); 519 (2%, $[SnNeof_3]^+$); 489 (100%, $[M - Neof]^+$, Sn-pattern); 464 (9%, Sn-pattern); 433 (3%, Sn-pattern); 421 (1%, Sn-pattern); 385 (1%, $[SnNeof_2]^+$); 377 (3%, Sn-pattern); 355 (1%, $[M - Neof_2]^+$, Sn-pattern); 253 (4%, $[SnNeof]^+$); 223 (14%, $[M - Neof_3]^+$, Sn-pattern); 197 (15%, Sn-pattern); 118 (5%, $[Sn]^+$); 103 (9%, $[M - SnNeof_3]^+$).

*3.2.1.12. (E)-3-trineophyltin–2-propenol (**13**).* MS (*m*/*z*, relative intensity): 576 (M^+; Sn-pattern); 519 (7%, $[SnNeof_3]^+$); 443 (100%, $[M - Neof]^+$, Sn-pattern); 403 (22%, Sn-pattern); 385 (19%, $[SnNeof_2]^+$); 253 (15%, $[SnNeof]^+$); 197 (31%, Sn-pattern); 177 (5%, $[M - Neof_3]^+$, Sn-pattern); 133 (13%, $[Neof]^+$); 117 (5%, $[Sn]^+$); 57 (1%, $[M - SnNeof_3]$).

*3.2.1.13. 2-Trineophyltin–2-propenol (**14**).* MS (*m*/*z*, relative intensity): 576 (M^+; Sn-pattern); 519 (11%, $[SnNeof_3]^+$); 443 (100%, $[M - Neof]^+$, Sn-pattern); 403 (20%, Sn-pattern); 385 (17%, $[SnNeof_2]^+$); 253 (13%, $[SnNeof]^+$); 197 (34%, Sn-pattern); 177 (7%, $[M - Neof_3]^+$, Sn-pattern); 133 (12%, $[Neof]^+$); 118 (4%, $[Sn]^+$); 57 (2%, $[M - SnNeof_3]^+$).

*3.2.1.14. (E)-trineophyltin-1,2-diphenylethylene (**15**).* MS (*m*/*z*, relative intensity): 696 (M^+; Sn-pattern); 565 (100%, $[M - Neof]^+$, Sn-pattern); 519 (38%, $[SnNeof_3]^+$); 431 (1%, $[M - Neof_2]^+$, Sn-pattern); 385 (1%, $[SnNeof_2]^+$); 297 (15%, $[M - Neof_3]^+$, Sn-pattern); 253 (9%, $[SnNeof]^+$); 197 (41%, Sn-pattern); 177 (13%, $[M - SnNeof_3]^+$); 133 (7%, $[Neof]^+$); 118 (4%, $[Sn]^+$).

*3.2.1.15. (E)-2-trineophyltin-3-phenyl-2-propenol (**16**).* MS (*m*/*z*, relative intensity): 652 (M^+; Sn-pattern); 519 (100%, $[M - Neof]^+$, Sn-pattern); 463 (9%, Sn-pattern); 421 (5%, Sn-pattern); 405 (1%, Sn-pattern); 387 (2%, $[M - Neof_2]^+$, Sn-pattern); 351 (1%, Sn-pattern); 329 (1%, Sn-pattern); 275 (3%, Sn-pattern); 253 (11%, $[SnNeof_3]^+$); 235 (6%, Sn-pattern); 197 (25%, Sn-pattern); 133 (24%, $[M - SnNeof_3]^+$); 119 (5%, $[Sn]^+$); 55 (29%, $[C_3H_3O]^+$).

*3.2.1.16. (E)-3-trineophyltin-3-phenyl-2-propenol (**17**).* MS (*m*/*z*, relative intensity): 652 (M^+; Sn-pattern); 519 (52%, $[M - Neof]^+$, Sn-pattern); 403 (34%, Sn-pattern); 385 (15%, $[M - Neof_2]^+$, Sn-pattern); 253 (13%, $[M - Neof_3]^+$, Sn-pattern); 197 (25%, Sn-pattern); 133 (14%, $[M - SnNeof_3]^+$); 117 (7%, $[Sn]^+$); 55 (20%, $[C_3H_3O]^+$).

*3.2.1.17. (E)-2-trineophyltin-2-butenol (**18**).* MS (*m*/*z*, relative intensity): 590 (M^+; Sn-pattern); 519 (6%, $[SnNeof_3]^+$); 457 (100%, $[M - Neof]^+$, Sn-pattern); 443 (14%, Sn-pattern); 324 (4%, $[M - Neof_2]^+$, Sn-pattern); 253 (23%, $[SnNeof]^+$); 197 (25%, Sn-pattern); 191 (12%, $[M - Neof_3]^+$, Sn-pattern); 133 (7%, $[Neof]^+$); 118 (4%, $[Sn]^+$); 105 (9%, $[C_8H_9]^+$); 55 (15%, $[C_3H_3O]^+$).

*3.2.1.18. (E)-3-trineophyltin-2-butenol (**19**).* MS (*m*/*z*, relative intensity): 590 (M^+; Sn-pattern); 519 (7%, $[SnNeof_3]^+$); 457 (100%, $[M - Neof]^+$, Sn-pattern); 401 (3%, Sn-pattern); 385 (2%, $[SnNeof_2]^+$); 345 (3%, Sn-pattern); 253 (4%, $[SnNeof]^+$); 197 (14%, Sn-pattern); 133 (5%, $[Neof]^+$); 118 (2%, $[Sn]^+$); 55 (8%, $[C_3H_3O]^+$).

*3.2.1.19. 2-Trineophyltin-2-propenoic acid methyl ester (**20**).* MS (*m*/*z*, relative intensity): 604 (M^+; Sn-pattern);519 (62%, $[SnNeof_3]^+$); 471 (100%, $[M - Neof]^+$, Sn-pattern); 385 (3%, $[SnNeof_2]^+$); 338 (3%, $[M - Neof_2]^+$, Sn-pattern); 253 (12%, $[SnNeof]^+$); 205 (2%, $[M - Neof_3]^+$, Sn-pattern); 133 (8%, $[Neof]^+$); 118 (4%, $[Sn]^+$).

*3.2.1.20. (E)-3-trineophyltin-3-phenyl-2-propenoic acid methyl ester (**21**).* MS (*m*/*z*, relative intensity): 680 (M^+; Sn-pattern); 547 (62%, $[M - Neof]^+$, Sn-pattern); 519 (5%, $[SnNeof_3]^+$); 415 (11%, $[M - Neof_2]^+$, Sn-pattern); 385 (29%, $[SnNeof_2]^+$); 281 (6%, $[M - Neof_3]^+$, Sn-pattern); 253 (10%, $[SnNeof]^+$); 197 (21%, Sn-pattern); 149 (13%, Sn-pattern); 133 (14%, $[Neof]^+$); 118 (6%, $[Sn]^+$); 105 (11%, $[C_8H_9]^+$).

*3.2.1.21. (E)-2-trineophyltin-3-phenyl-2-propenoic acid methyl ester (**22**).* MS (*m*/*z*, relative intensity): 680 (M^+; Sn-pattern); 547 (100%, $[M - Neof]^+$, Sn-pattern); 519 (73%, $[SnNeof_3]^+$); 415 (2%, $[M - Neof_2]^+$, Sn-pattern); 385 (4%, $[SnNeof_2]^+$); 281 (17%, $[M - Neof_3]^+$, Sn-pattern); 253 (11%, $[SnNeof]^+$); 197 (29%, Sn-pattern); 149 (9%, Sn-pattern); 133 (9%, $[Neof]^+$); 118 (3%, $[Sn]^+$); 105 (9%, $[C_8H_9]^+$).

Acknowledgements

This work was supported by grants from CONICET (Capital Federal, Argentina) and Universidad Nacional del Sur (Bahía Blanca, Argentina). The generous help of Professor M. González Sierra (IQUIOS, Rosario, Argentina) and Professor T.N. Mitchell and P. Urschel (Dortmund University, Dortmund, Germany) in obtaining the NMR spectra and Mass spectra is acknowledged. A travel grant to one of us (JCP) from the Alexander von Humboldt Foundation, and a fellowship from CONICET and at present from DAAD (Germany) to VID are also gratefully acknowledged.

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