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Stereoselective hydrostannation of substituted alkynes initiated by triethylborane and reactivity of bulky triorganotin hydrides

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Abstract

This paper reports the results obtained in a study on the radical hydrostannation of mono- and disubstituted alkynes with bulky triorganotin hydrides using triethylborane as initiator. The addition of trineophyl- (**1**), tris[(phenyldimethylsilyl)methyl]- (**2**), and 9-triptycyldimethyltin (**3**) hydride to eight alkynes was carried out at room temperature leading to vinylstannanes in good to excellent yields and, mostly, with complete stereoselectivity. The results obtained in a study on the relative reactivity of trineophyl- (**1**), tris[(phenyldimethylsilyl)methyl]- (**2**), 9-triptycyldimethyltin (**3**) hydrides, and tri-*n*-butyltin hydride (**29**) using the radical reactions between these hydrides and 6-bromo-1-hexene (**28**) are also reported. Full ^{1}H-, ^{13}C-, and ^{119}Sn NMR characteristics are included.

Keywords: Radical hydrostannations; Triethylborane; Vinylstannanes; Stereoselectivity; Bulky organotin hydrides reactivity

1. Introduction

Organotin hydrides are versatile reagents for organic synthesis. They have found wide application not only as reducing reagents but also as intermediates in the generation of carbon–carbon bonds, and for the preparation of vinylstannanes, invaluable starting materials for cross-coupling reactions [1]. The radical addition of organotin hydrides to alkynes induced by triethylborane reported by Oshima and co-workers permits stereoselective hydrostannations at room temperature and even at low temperatures such as −78 °C [2]. In previous studies we have shown that the size of the organic ligands attached to the tin atom affects not only the reactivity but also the stereoselectivity of the reactions of these compounds [3]. These studies included the synthesis of vinylstannanes containing organotin moieties with neophyl, (phenyldimethylsilyl)methyl, and 9-triptycyl ligands attached to the tin atom, via radical hydrostannation using azobisisobutyronitrile (AIBN) as a radical initiator [3f,3g,3h,3i].

In order to compare the stereoselectivities that can be achieved using triethylborane as initiator with those obtained using AIBN, we now considered it convenient to carry out a study on the radical addition of the bulky trineophyl- (**1**), tris[(phenyldimethylsilyl)methyl]- (**2**), and 9-triptycyldimethyltin (**3**) hydrides to alkynes mediated by triethylborane. We also considered it of interest to carry out a study of the relative reactivity of these hydrides under radical conditions.

2. Results and discussion

The addition of trineophyl- (**1**), tris[(phenyldimethylsilyl)methyl]- (**2**), and 9-triptycyldimethyltin hydride (**3**) to phenylacetylene, propargyl alcohol, methyl propiolate,

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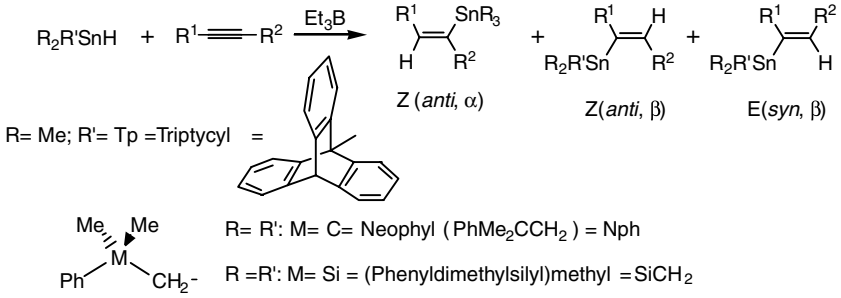
3-butyn-2-one, diphenylacetylene, methyl and ethyl phenylpropiolates, and dimethyl acetylenedicarboxylate was carried out at room temperature, in toluene, under a nitrogen atmosphere, using an organotin hydride/alkyne ratio of 1:1, and 0.1 equiv. of triethylborane. Taking into account previous work [3f,3g,3h,3i], we considered it possible that under radical conditions the main products of these reactions should be those corresponding to an anti-addition of the tin hydride, $Z(\alpha)$ and $Z(\beta)$, as shown in the scheme included in Table 1. The results obtained are summarized in Table 1.

The NMR characteristics of compounds **4**, **7**, **11**, **17**, **19**, **25** [3f], **8**, **12**, **23** [3g], **14** [3h], and **6**, **13**, **18**, **21**, **27** [3i], have been reported in earlier publications of our research group. ^{13}C- and ^{1}H NMR characteristics of the new organotins **5**, **10**, **15**, **16**, **20**, **22**, **24**, **26**, are summarized in Tables 2 and 3.

The *Z* stereochemistry of adducts **5**–**8**, **10**–**24**, and **26**–**27** was assigned taking into account that the observed $^{3}J(^{119}Sn, ^{1}H)$ coupling constants in the ^{1}H NMR spectra were mostly well over 100 Hz, which indicate the existence of *trans* H–C–C–Sn linkages in these compounds. On the other hand, the observed $^{3}J(^{119}Sn, ^{1}H)$ coupling constants for compounds **4** (64.0 Hz [3f]) and **25** (85.2 Hz [3f]), clearly indicate the existence of a *cis* H–C–C–Sn linkage in these adducts. It should be noted that although we were not able to obtain compound **9** in a pure state, in the ^{1}H NMR of the crude products it is possible to observe the coupling constants $^{3}J(^{119}Sn, ^{1}H)_{trans}$ 151.0 Hz and $^{3}J(^{119}Sn, ^{1}H)_{cis}$

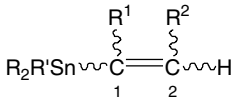
Table 1
Trineophyl- (**1**), tris(phenyldimethylsilylmethyl)- (**2**), and 9-tripticyldimethyltin hydride (**3**) radical additions to substituted alkynes



Entry No.	Compound No.	R_2R'	R^1	R^2	Time (h)	$Z(\beta)$ (%)	$Z(\alpha)$ (%)	$E(\beta)$ (%)	Yield[a] (%)	^{119}Sn[b] (ppm)
1	**4**	Nph	H	Ph	1	–	–	100	100	−93.7
2	**5**	$SiCH_2$	H	Ph	3	100	–	–	91	−34.4
3	**6**	$TpMe_2$	H	Ph	1	100	–	–	98	−76.9
4	**7**	Nph	H	CH_2OH	3	100	–	–	64	−97.5
5	**8** and **9**	$SiCH_2$	H	CH_2OH	2	67 (**8**)	33 (**9**)[c,d]	–	55[e]	**8**: −40.4 **9**: −37.8
6	**10**	$TpMe_2$	H	CH_2OH	1	100	–	–	50	−78.9
7	**11**	Nph	H	COOMe	1	100	–	–	100	−92.4
8	**12**	$SiCH_2$	H	COOMe	2	100	–	–	93	−37.3
9	**13**	$TpMe_2$	H	COOMe	1.5	100	–	–	98	−75.1
10	**14**	Nph	H	COMe	3[f]	100[f]	–	–	79[f]	−89.0[f]
11	**15**	$SiCH_2$	H	COMe	3	100	–	–	100	−37.2
12	**16**	$TpMe_2$	H	COMe	24	–	100[d]	–	74	−74.2
13	**17**	Nph	Ph	Ph	24	100[h]	–	–	40	−89.0
14	–	$SiCH_2$	Ph	Ph	24	–	–	–	[g]	–
15	**18**	$TpMe_2$	Ph	Ph	1	100[h]	–	–	63	−66.9
16	**19**	Nph	Ph	COOMe	5	100	–	–	87	−81.7
17	**20**	$SiCH_2$	Ph	COOMe	2	100	–	–	85	−21.0
18	**21**	$TpMe_2$	Ph	COOMe	2	100	–	–	83	−64.8
19	**22**	Nph	Ph	COOEt	1	100	–	–	86	−80.8
20	**23**	$SiCH_2$	Ph	COOEt	2	100	–	–	92	−23.7
21	**24**	$TpMe_2$	Ph	COOEt	2	100	–	–	53	−66.3
22	**25**	Nph	COOMe	COOMe	24	–	–	100	90	−80.7
23	**26**	$SiCH_2$	COOMe	COOMe	1	100[h]	–	–	100	−17.1
24	**27**	$TpMe_2$	COOMe	COOMe	2	100[h]	–	–	73	−58.4

[a] Yields of products isolated from the column chromatography.
[b] In $CDCl_3$; in ppm with respect to Me_4Sn.
[c] From the ^{1}H- and ^{119}Sn NMR of the crude products mixture.
[d] In this case isomer α.
[e] There is some decomposition during purification and compound **9** could not be separated pure.
[f] From [3h].
[g] No adduct formed.
[h] In these cases $Z(\beta) = Z(\alpha)$.

Table 2
^{13}C NMR data of vinyltin adducts **5**, **10**, **15**, **16**, **20**, **22**, **24**, **26**[a]



No.	R_2R'[b]	R^1	R^2	C(1) [^1J(Sn,C)]	C(2) [^2J(Sn,C)]	R^{1c} [^2J(Sn,C)]	R^{2c} [^3J(Sn,C)]	Other signals
5	$SiCH_2$	H	Ph	134.64 (333.9)	146.44 (25.4)	–	140.37 (30.6)	[d]
10	$TpMe_2$	H	CH_2OH	129.70 (341.1)	144.84 (31.3)	–	64.49 (39.8)	[e]
15	$SiCH_2$	H	COMe	130.82 (342.7)	158.56 (41.8)	–	197.51 (26.2)	[f]
16	$TpMe_2$	COMe	H	156.11 (325.2)	139.0 (30.4)	198.0 (23.0)	–	[g]
20	$SiCH_2$	Ph	COOMe	140.02 (390.1)	154.60 (11.0)	141.23 (22.2)	170.10 (40.5)	[h]
22	Nph	Ph	COOEt	141.72 (304.9)	152.30 (7.3)	151.79 (32.7)	171.96 (35.8)	[i]
24	$TpMe_2$	Ph	COOEt	139.59 (nd)	155.61 (27.2)	138.45 (23.6)	171.32 (38.6)	[j]
26	$SiCH_2$	COOMe	COOMe	162.38 (358.4)	134.29 (29.4)	167.00 (20.4)	171.68 (43.8)	[k]

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to TMS; $^nJ(^{119}Sn, ^{13}C)$ coupling constants, in Hz (in brackets); nd = not determined.
[b] $R_2R' = SiCH_2$ = tris(phenyldimethylsilylmethyl); $R_2R' = TpMe_2$ = triptycyldimethyl.
[c] Chemical shifts of the carbons attached to C(1) and C(2).
[d] −2.82 (258.3) (51.7); −0.06 (13.0) (51.9); 127.05; 127,55; 127,81; 128.09; 128.55; 133.22; 141.21 (20.5).
[e] −4.67 (342.2); 53.30 (nd); 54.93; 123.88; 124.62; 124.66; 125.44 (30.8); 148.17; 148.58.
[f] −2.49 (279.1) (48.5); 0.20 (13.9) (52.9); 30.09; 127.51; 128.44; 133.29; 141.62 (20.8).
[g] −6.58 (nd); 28.68; 29.31; 54.0 (nd); 123.04; 123.72; 123.75; 124.38 (29.7); 147.50; 149.91.
[h] −1.28 (272.2) (48.6); 0.00 (13.0) (51.8); 51.58; 127.53; 128.22; 128.35; 128.52; 133.24; 137.85 (22.1).
[i] 14.30; 32.40 (32.7); 33.41 (336.9); 37.96 (18.5); 60.66; 125.25; 125.35; 127.85; 128.05; 128.28; 128.34; 138.67 (17.5).
[j] −2.62 (361.3); 11.76; 54.78; 57.21 (nd); 60.60; 123.58; 124.31; 124.67; 126.19 (32.3); 128.17; 128.37; 128.86; 147.60; 147.68.
[k] −1.38 (291.7) (49.1); −0.08 (14.8) (53.1); 51.72; 51.89; 127.46; 128.61; 133.27; 141.16 (21.2).

Table 3
^1H NMR data of vinyltin compounds **5**, **10**, **15**, **16**, **20**, **22**, **24**, **26**

No.	Chemical shifts (δ, in ppm)[a]
5	−0.07 [s, 6H, ^2J(Sn,H) 75.8]; 0.26 (s, 18H); 6.14 [d, 1H, ^3J(H,H) 14.0; ^2J(Sn,H) 68.0]; 7.17–7.50 (m, 20H); 7.53 [d, 1H, ^3J(H,H) 14.0; ^3J(Sn,H) 160.0]
10	0.65 [s, 6H, ^2J(Sn,H) 57.0]; 4.41 (2H); 5.29 (s, 1H); 6.32 [dt, 1H, ^3J(H,H) 12.9, ^4J(Sn,H) 1.8, ^2J(Sn,H) 80.5]; 6.68 [dt, 1H, ^3J(H,H) 12.9, ^3J(H,H) 4.2, ^3J(Sn,H) 126.6]; 6.82–7.40 (m, 12H)
15	0.01 [s, 6H, ^2J(Sn,H) 75.0]; 0.20 (s, 18H); 2.09 (s, 3H); 6.86 (d, 1H, ^3J(H,H) 12.0; ^2J(Sn,H) 86.0]; 6.91 [d, 1H, ^3J(H,H) 12.0, ^3J(Sn,H) 162.0]; 7.28–7.43 (m, 15H)
16	0.67 [s, 6H, ^2J(Sn,H) 57.0]; 2.37 (s, 3H); 5.30 (s, 1H); 6.05 [d, 1H, ^2J(H,H) 1.0, ^2J(Sn,H) 66.4]; 6.74 [d, 1H, ^2J(H,H) 1.0, ^3J(Sn,H) 141.0]; 6.85–7.38 (m, 12H)
20	0.03 [s, 6H, ^2J(Sn,H) 76.0]; 0.25 (s, 18H); 3.71 (s, 3H); 7.24–7.48 (m, 20H); 8.44 [s, 1H, ^3J(Sn,H) 122.0];
22	1.04 (s, 18H); 1.09 [s, 6H, ^2J(Sn,H) 53.0]; 1.27 [t, 3H, ^3J(H,H) 7.0]; 4.14 [q, 2H, ^3J(H,H) 7.0]; 7.01–7.27 (m, 20H); 8.14 [s, 1H, ^3J(Sn,H) 107.8]
24	0.00 [t, 3H, ^3J(H,H) 7.2]; 0.67 [s, 6H, ^2J(Sn,H) 54.2]; 3.33 [q, 2H, ^3J(H,H) 7.2]; 5.49 (s, 1H); 6.95–7.77 (m, 17H); 8.73 [s, 1H, ^3J(Sn,H) 122.4]
26	0.00 [s, 6H, ^2J(Sn,H) 78.6]; 0.07 (s, 18H); 3.42 (s, 3H); 3.62 (s, 3H); 6.43 [s, 1H, ^3J(Sn,H) 100.0]; 7.08–7.51 (m, 15H)

Multiplicity and J values in parentheses.
$^nJ(^{119}Sn, ^1H)$ coupling constants in Hz.
[a] In $CDCl_3$.

73.5 Hz corresponding to the α stereoisomer. These structures were confirmed by other ^{13}C- and ^1H NMR data.

In Table 1 it can be seen that only in the case of the reaction between diphenylethyne and tris[(phenyldimethylsilyl)methyl]tin hydride (**2**) (entry 14) could we not detect any reaction product after 24 h. The results summarized in Table 1 clearly demonstrate the high regio- and stereoselectivities that can be obtained in these radical hydrostannations using bulky organotin hydrides. Thus, the additions of hydrides **1**, **2**, and **3** to mono- and disubstituted alkynes (Table 1, entries 1–24) lead in 22 out of 23 cases to one diastereoisomer and in just one case -entry 5- to a mixture of two stereoisomers. Also in 21 cases (entries 2–13, 15–21, and 23–24) the main (entry 5) or sole products are those with $Z(\beta)$ or $Z(\alpha)$ (entry 12) configuration, i.e., the products resulting from an anti-attack.

The formation of the E-adducts **4** and **25**, entries 1 and 22, could be explained by 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 [4,5]. On the other hand, the formation of the Z-vinylstannanes has been explained by considering that in the equilibrium mixture of the conformers corresponding to the intermediate alkyl radicals – the products of the addition of a second organotin radical – the conformers that

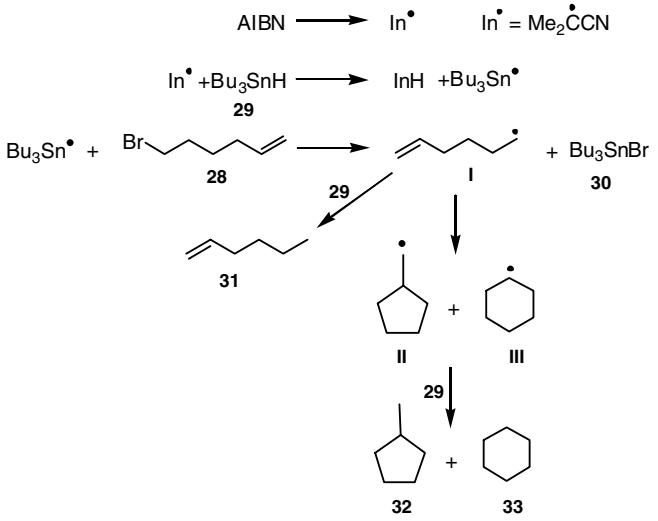
lead via anti-elimination of the organotin radical to the *Z*-vinylstannanes are present in higher concentration. This has been ascribed to the favorable interaction between the tin atom and the neighbouring groups that predominates over the opposing effect of greater steric hindrance [5].

These results clearly demonstrate that, contrary to what has previously been stated [4,6,7], it is possible to carry out stereoselective radical hydrostannations of alkynes using organotin hydrides. Thus, excellent stereoselectivities could be achieved at room temperature using triethylborane as radical initiator and organotin hydrides with bulky organic ligands such as **1**, **2**, and **3**.

As for the radical initiator, the results obtained show that, generally speaking, there are no significant differences in the stereoselectivities and the yields obtained using either AIBN or triethylborane. However, in some cases we have found some differences. Thus, whereas in the case of the addition of trineophyltin hydride (**1**) to methyl propiolate and 3-butyn-2-one the reactions initiated by AIBN lead to mixtures of two adducts [3f,3h], the additions to the same substrates mediated by triethylborane (Table 1, entries 7 and 10) lead to just one stereoisomer. Also, whereas we could not detect any adduct in the reaction of triptycyldimethyltin hydride (**2**) with propargyl alcohol and 3-butyn-2-one initiated by AIBN [3i], the hydrostannation of the same substrates with **2** mediated by triethylborane takes place smoothly to give one stereoisomer (Table 1, entries 6 and 12).

Taking into account the synthetic importance of the tin hydrides with bulky organic ligands, we considered it of interest to determine the relative reactivities of trineophyl- (**1**), tris[(phenyldimethylsilyl)methyl]- (**2**), and 9-triptycyldimethyltin hydride (**3**). In order to compare the relative reactivity of organotin hydrides, we had in previous studies used the reaction between the hydrides and carbon tetrachloride. We measured the time required for the hydrides to react completely at a known concentration in carbon tetrachloride (0.0077 M). These reactions were followed by IR spectroscopy by observing the disappearance of the Sn–H absorption ([3e], and references therein cited). We now considered it possible to achieve a better approximation to the estimation of the relative reactivities of the organotin hydrides by studying the composition of the mixture of products resulting from their reaction with 6-bromo-1-hexene (**28**) under radical conditions. Thus, it is known that the free radical reaction between **28** and tributyltin hydride (**29**) leads to a mixture of three compounds: 1-hexene (**31**), methylcyclopentane (**32**), and cyclohexane (**33**), as shown in Scheme 1 [8].

The 5-hexenyl radical (**I**) has been used as a radical probe due to its rapid rate of cyclization ($1.3 \times 10^5\ s^{-1}$) to the cyclopentylmethyl radical (**II**) and the cyclohexyl radical (**III**) [9]. The less thermodynamically stable radical **II** is rapidly formed via a non-symmetrical transition state more sterically favorable for the formation of the 5 membered ring. A characteristic feature of the cyclizations to give radicals **II** and **III** is that they are irreversible at the working temperatures (−80 to 120 °C) [9].



Scheme 1. Reaction of 6-bromo-1-hexene with tributyltin hydride under free radical conditions.

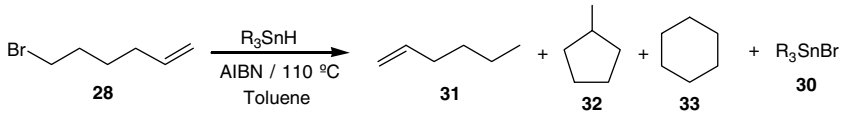
Taking into account the previous discussion, we carried out a study of the reaction of 6-bromo-1-hexene (**28**) with trineophyl- (**1**), tris[(phenyldimethylsilyl)methyl]- (**2**) [3g], and 9-triptycyldimethyltin hydride (**3**) [3i], and also tributyltin hydride (**29**). The reactions were carried out using three concentrations of the hydrides (0.1, 0.3 and 0.5 M) in toluene, at 110 °C, during 3 h and in the presence of catalytic amounts of AIBN. The relative ratios of the products were determined by GC–MS analysis. The results obtained are summarized in Table 4.

These results indicate that at 0.1 M concentration, the reactivity of hydrides **1** and **2** is almost the same as that of tributyltin hydride (**29**), and that these three hydrides undergo hydrogen abstraction by the 5-hexenyl radical (**I**) about twice as fast as does hydride **3**. Also, while the yield of the cyclization products (**32** + **33**) obtained using hydride **3** reach 93%, the yields obtained using hydrides **29**, **1**, and **2** are around 83%. The latter would confirm that triptycyldimethyltin hydride (**3**) is less reactive than the others because the slower hydrogen abstraction rate by the radical **I** gives more time for the cyclization to give **II** and **III**.

Using higher concentrations (0.3 and 0.5 M) it can be seen that, as expected, all four hydrides undergo faster hydrogen abstraction. However, it should be noted that while the increase of the concentration from 0.3 to 0.5 M in the case of hydrides **29** and **1** leads to an increase in the rate of hydrogen abstraction, in the case of hydrides **2** and **3** the rates remain almost constant as shown by the amounts of open chain (**31**) and cyclization products (**32** + **33**) obtained for both concentrations.

From these results it is possible to conclude that the decreasing order for the rate of the hydrogen abstraction step from these hydrides to radical **I** is:

Table 4
Radical reactions of 6-bromo-1-hexene with triorganotin hydrides **1**, **2**, **3**, and **29**



28 **31** **32** **33** **30**

R_3SnH	**31** (%)	**32** (%)	**33** (%)	**30** (%)[a]
Concentration: 0.1 M				
Bu_3SnH (**29**)	16	78	6	95
$Neoph_3SnH$ (**1**)[b]	17	76	7	94
$(PhSiMe_2CH_2)_3SnH$ (**2**)	17	78	5	93
$TripMe_2SnH$ (**3**)[b]	7	88	5	99
Concentration: 0.3 M				
Bu_3SnH (**29**)	29	67	4	96
$Neoph_3SnH$ (**1**)	26	70	4	95
$(PhSiMe_2CH_2)_3SnH$ (**2**)	23	74	3	97
$TripMe_2SnH$ (**3**)	20	75	5	94
Concentration: 0.5 M				
Bu_3SnH (**29**)	48	49	3	98
$Neoph_3SnH$ (**1**)	37	59	4	98
$(PhSiMe_2CH_2)_3SnH$ (**2**)	22	72	6	96
$TripMe_2SnH$ (**3**)	21	72	7	97

Trip = Triptycyl.
[a] Isolated triorganotin bromide.
[b] Neoph = Neophyl = $PhCMe_2CH_2$.

$$Bu_3SnH > Neoph_3SnH > (PhSiMe_2CH_2)_3SnH > TripMe_2SnH$$

The results obtained using a 0.5 M concentration could indicate that tributyltin hydride (**29**) would undergo hydrogen abstraction 1.3 times faster than hydride **1**, 2.2 times faster than hydride **2**, and 2.3 times faster than hydride **3**. These results also reflect the great effect upon the reactivity obtained by for example replacing one small organic ligand such as the methyl group of the trimethyltin hydride by the bulkier tripticyl ligand.

3. Experimental

3.1. General methods

NMR spectra were obtained using a Bruker ARX 300 instrument. Mass spectra were obtained using a Finnigan MAT Model 8230 at Dortmund University (Germany). Infrared spectra were recorded with a Nicolet Nexus FT spectrometer. Elemental analyses (C, H) were performed at Dortmund University. All the solvents and reagents used were analytical reagent grade. Trineophyl- (**1**) [10], tris [(phenyldimethylsilyl)methyl]- (**2**) [3g] and 9-triptycyldimethyltin- (**3**) [3i] hydrides were prepared as described previously. Phenylacetylene, diphenylacetylene, propiolic acid, phenylpropiolic acid, acetylenedicarboxylic acid, propargyl alcohol, 3-butyn-2-one, and triethylborane were purchased and purified by common procedures before use. The esters of the acids were obtained following known techniques [11].

3.2. Addition of triorganotin hydrides *1–3* to substituted alkynes under radical conditions

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

To a solution of propargyl alcohol (0.047 g, 0.80 mmol) and tin hydride **3** (0.340 g, 0.80 mmol) in dry toluene (3 mL) under nitrogen, was added triethylborane (0.080 mmol, 0.080 mL of a 1 M solution in hexane), and the mixture was stirred for 1 h at room temperature. The solvent was then distilled off under reduced pressure. The ^{119}Sn NMR spectrum of the product showed that it consisted of only one compound: (*Z*)-3-triptycyldimethylstannyl-2-propen-1-ol (**10**), peak at −78.9 ppm. Column chromatography (silica gel 60) of the crude product gave compound **10** pure (0.184 g, 0.40 mmol, 50%) in the fraction eluted with hexane–diethyl ether (96:4).

3.3. Reaction of 6-bromo-1-hexene (*28*) with triorganotin hydrides (*1–3, 29*)

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

To a 0.1 M solution of tin hydride **3** (0.20 g, 0.50 mmol) in dry toluene (5 mL) under argon was added 6-bromo-1-hexene (0.081 g, 0.50 mmol) and AIBN as a catalyst. The mixture was heated under reflux for 3 h. A solution of volatile compounds in toluene was obtained by distillation. Reaction products were identified by GC–MS in a Hewlett–Packard

CGL-Ms 6890/5972 (capillary column HP5-Ms 30 m × 0.25 mm × 0.25 μm) using the corresponding patterns (see Table 4).

3.4. Mass spectra and elemental analyses of the new vinyltin compounds

3.4.1. (Z)-1-tris[(phenyldimethylsilyl)methyl]stannyl-2-phenylethene (5)

MS (*m*/*z*, rel. int.): 570 (3%, $[Sn(CH_2Si(CH_3)_2Ph)_3]^+$, Sn-pattern); 521 (100%, $[M-(CH_2Si(CH_3)_2Ph)]^+$, Sn-pattern); 453 (5%, Sn-pattern); 420 (2%, $[Sn(CH_2Si(CH_3)_2Ph)_2]^+$, Sn-pattern); 315 (21%, Sn-pattern); 270 (11%, $[SnCH_2Si(CH_3)_2Ph]^+$, Sn-pattern); 253 (17%, Sn-pattern); 223 (17%, $[C_8H_7Sn]^+$, Sn-pattern); 197 (17%, Sn-pattern); 150 (6%, $[CH_2Si(CH_3)_2Ph]^+$); 136 (34%, $[Si(CH_3)_2Ph]^+$); 120 (15%, $[Sn]^+$, Sn-pattern); 77 (2%, $[C_6H_5]^+$). Anal. Calc. for $C_{35}H_{46}Si_3Sn$: C, 62.77; H, 6.92. Found: C, 62.66; H, 6.78%.

3.4.2. (Z)-3-triptycyldimethylstannyl-2-propen-1-ol (10)

MS (*m*/*z*, rel. int.): 445 (6%, $[M-(CH_3)]^+$, Sn-pattern); 403 (5%, $[SnTrip(CH_3)_2]^+$, Sn-pattern); 373 (2%, $[SnTrip]^+$, Sn-pattern); 253 (100%, $[Trip]^+$); 150 (41%, $[Sn(CH_3)_2]^+$, Sn-pattern); 57 (69%, $[M-SnTrip(CH_3)_2]^+$). Anal. Calc. for $C_{25}H_{24}OSn$: C, 65.39; H, 5.27. Found: C, 65.78; H, 5.38%.

3.4.3. (Z)-4-[(tris(phenyldimethylsilyl)methyl)stannyl]-3-buten-2-one (15)

MS (*m*/*z*, rel. int.): 570 (4%, $[Sn(CH_2Si(CH_3)_2Ph)_3]^+$, Sn-pattern); 487 (100%, $[M-(CH_2Si(CH_3)_2Ph)]^+$, Sn-pattern); 453 (6%, Sn-pattern); 357 (10%, Sn-pattern); 337 (4%, $[M-(CH_2Si(CH_3)_2Ph)_2]^+$, Sn-pattern); 270 (9%, $[SnCH_2Si(CH_3)_2Ph]^+$, Sn-pattern); 227 (13%, Sn-pattern); 203 (25%); 197 (28%, Sn-pattern); 135 (53%, $[Si(CH_3)_2Ph]^+$); 120 (19%, $[Sn]^+$, Sn-pattern). Anal. Calc. for $C_{31}H_{44}OSi_3Sn$: C, 58.58; H, 6.98. Found: C, 58.65; H, 6.80%.

3.4.4. 3-triptycyldimethylstannyl-3-buten-2-one (16)

MS (*m*/*z*, rel. int.): 457 (22%, $[M-(CH_3)]^+$, Sn-pattern); 403 (5%, $[SnTrip(CH_3)_2]^+$, Sn-pattern); 373 (4%, $[SnTrip]^+$, Sn-pattern); 253 (75%, $[Trip]^+$); 219 (100%, $[M-Trip]^+$, Sn-pattern); 189 (17%, $[SnC_4H_5O]^+$, Sn-pattern); 135 (9%, $[SnCH_3]^+$, Sn-pattern); 120 (2%, $[Sn]^+$, Sn-pattern). Anal. Calc. for $C_{26}H_{24}OSn$: C, 66.27; H, 5.13. Found: C, 66.65; H, 5.34%.

3.4.5. (Z)-Methyl-3-[(tris(phenyldimethylsilyl)methyl)-stannyl]-3-phenylpropenoate (20)

MS (*m*/*z*, rel. int.): 579 (100%, $[M-CH_2Si(CH_3)_2Ph]^+$, Sn-pattern); 429 (21%, $[M-(CH_2Si(CH_3)_2Ph)_2]^+$, Sn-pattern); 420 (1%, $[Sn(CH_2Si(CH_3)_2Ph)_2]^+$, Sn-pattern); 279 (4%, $[(M-(CH_2Si(CH_3)_2Ph)_3]^+$ Sn-pattern); 270(6%, $[SnCH_2Si(CH_3)_2Ph]^+$, Sn-pattern); 227 (20%, Sn-pattern); 197 (7%, Sn-pattern); 150 (7%, $[CH_2Si(CH_3)_2Ph]^+$); 135 (19%, $[Si(CH_3)_2Ph]^+$); 120 (9%, $[Sn]^+$, Sn-pattern). Anal. Calc. for $C_{37}H_{48}O_2Si_3Sn$: C, 61.07; H, 6.65. Found: C, 60.96; H, 6.48%.

3.4.6. (Z)-Ethyl-3-trineophylstannyl-3-phenylpropenoate (22)

MS (*m*/*z*, rel. int.): 562 (100%, $[M-Neoph]^+$, Sn-pattern); 519 (75%, $[SnNeoph_3]^+$, Sn-pattern); 428 (3%, $[M-Neoph_2]^+$, Sn-pattern); 385 (7%, $[SnNeoph_2]^+$, Sn-pattern); 295 (20%, $[M-Neoph_3]^+$, Sn-pattern); 253 (14%, $[SnNeoph]^+$, Sn-pattern); 175 (28%, $[M-SnNeoph_3]^+$); 133 (9%, $[Neoph]^+$); 120 (3%, $[Sn]^+$, Sn-pattern); 105 (7%, $[C_8H_9]^+$). Anal. Calc. for $C_{41}H_{50}O_2Sn$: C, 71.00; H, 7.27. Found: C, 70.88; H, 7.10%.

3.4.7. Z-Ethyl-3-triptycyldimethylstannyl-3-phenylpropenoate (24)

MS (*m*/*z*, rel. int.): 579 (6%, (6%, $[M]^+$, Sn-pattern); 564 (20%, $[M-(CH_3)]^+$, Sn-pattern); 518 (12%, Sn-pattern); 403 (22%, $[SnTrip(CH_3)_2]^+$, Sn-pattern); 388 (18%, $[SnTripCH_3]^+$, Sn-pattern); 373 (10%, $[SnTrip]^+$, Sn-pattern); 325 (100%, $[M-Trip]^+$, Sn-pattern); 280 (30%, Sn-pattern); 253 (82%, $[Trip]^+$); 150 (11%, $[Sn(CH_3)_2]^+$, Sn-pattern); 120 (2%, $[Sn]^+$, Sn-pattern). Anal. Calc. for $C_{33}H_{30}O_2Sn$: C, 68.66; H, 5.24. Found: C, 68.30; H, 4.90%.

3.4.8. (Z)-2-[(tris(phenyldimethylsilyl)methyl)stannyl]-butenedioic acid dimethylester (26)

MS (*m*/*z*, rel. int.): 561 (100%, $[M-CH_2Si(CH_3)_2Ph]^+$, Sn-pattern); 452 (20%, Sn-pattern); 289 (12%, Sn-pattern); 261 (12%, $[SnC_6H_7O_4]^+$, Sn-pattern); 227 (31%, Sn-pattern); 197 (13%, Sn-pattern); 150 (21%, $[CH_2Si(CH_3)_2Ph]^+$; 135 (43%, $[Si(CH_3)_2Ph]^+$; 120 (20%, $[Sn]^+$, Sn-pattern); 105 (8%, $[Si(C_6H_5]^+$); 59 (4%, $[C_2H_3O_2]^+$). Anal. Calc. for $C_{33}H_{46}O_4Si_3Sn$: C, 55.85; H, 6.53. Found: C, 55.70; H, 6.62%.

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