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On the chemospecificity of the double stannylation and double hydrostannation of terminal alkynes by the tributylstannane in the presence of thiol

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Abstract

The mechanism of competing double stannylation and double hydrostannation reactions of terminal alkynes in the presence of arylthiol has been investigated. The data reveal the radical character of the reactions, the importance of the [tributylstannane/arylthiol] system as radical initiator *at ambient temperature* and the occurrence of a polarity reversal catalysis process in the double hydrostannation pathway. © 1997 Elsevier Science S.A.

Keywords: Double stannylation; Double hydrostannation; Propargylic compounds; Thiols

1. Introduction

In the course of recent preparative studies connected with the known ability of tin to undergo a variety of useful transformations, we recently reported on the arylthiol-promoted addition of tributylstannane to acetylenic bonds leading either to double hydrostannation or double stannylation according to experimental conditions [1]. Thus, it was pointed out that in the presence of small amounts of *p*-thiocresol, hydrostannation of propargyl *p*-tolyl ethers and amines promotes *at ambient temperature* the stereospecific formation of unsaturated [Z]-α,β-2/1 double stannylation adducts, whereas an increase in the catalyst amount leads to a drastic change in the course of the reaction: double hydrostannation takes place instead of double stannylation, leading to the formation of saturated β,β-2/1 adducts. In addition, the double hydrostannation process appears to be strongly dependent on the nature of the thiol. Best results in achieving a quasi-total selectivity towards gem-distannyl compounds were obtained using 4-methoxybenzenethiol thanks to its low homolytic bond dissociation energy [2]. Hereby, we successfully hydrostannate oxygenated and aminated propargylic substrates (Scheme 1), as well as numerous related compounds (see Table 1, Section 3) having significant synthetic potentialities.

Everything being equal, while the addition of stannane to alkynes could be specifically directed to the double hydrostannation, it is quite interesting to note the completely different behavior of propargyl phenyl sulfides, which are unable to undergo the double hydrostannation and lead to the double stannylation whatever the nature and the amount of catalyst (Scheme 2).

The presence of an aromatic ring on the sulfur atom is essential for double stannylation and it should be stressed that replacement of the aryl substituent by alkyl or cyclohexyl ones gives rise to the formation of standard monohydrostannylated α and β alkenes, without the appearance of any trace of double stannylation adducts.

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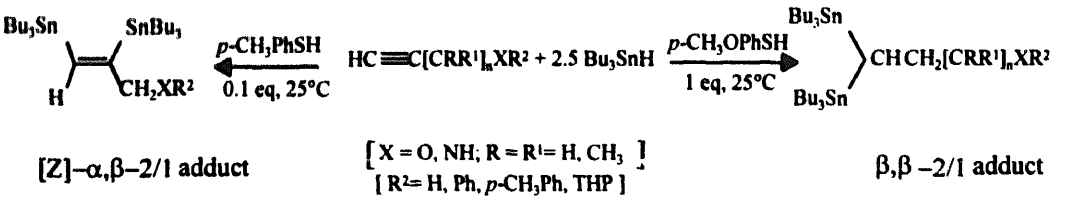


Scheme 1.

Obviously, the key to this lies in the mechanism involved and it prompted us to study the factors governing the chemospecificity of this reaction.

2. Results and discussion

Tin radical addition to ω-alkynyl phenyl sulfides has been recently studied by Montevecchi et al. [3], who investigated the feasibility of an intramolecular cyclisation of the intermediate thioalkyl-substituted β-(tributylstannyl)vinyl radicals of the type $Ph(CH_2)_nS(CH_2)_mC{=}CHSnBu_3$ onto the adjacent phenyl ring to obtain stannylated sulfur-containing heterocycles. The behaviour of these radicals has been reported to strongly depend on the characteristics of the side chain since intramolecular S_H2 reactions, 5-exo cyclisations or β-fragmentation reactions [4] could occur.

Hence, it is well established that interaction of stannyl radicals generated by the standard tributylstannane approach [5] on alkynyl sulfides involves the formation of monohydrostannylated vinyl radical intermediates as the reaction key step and constitutes cogent evidence that double hydrostannation and double stannylation reactions would involve an alternative fate of such radicals. Thus, the drastic change observed in the course of the reaction in our experimental conditions, i.e., *at ambient temperature and in the presence of thiol as catalyst*, would result from a synergistic effect due to the above-mentioned intrinsic properties of the sulfur-containing vinyl radicals relative to corresponding oxygen and nitrogen systems, associated with a likely different 'catalytic' behaviour of the arylthiol in the two pathways.

The free-radical addition mechanism just outlined predicts that addition of stannyl radicals onto appropriate monohydrostannylated compounds has to be initiated both *at ambient temperature and in the absence of standard radical initiators*. Obviously, the fact that the reactions do not occur in the absence of arylthiol shows that the initiation step does not happen spontaneously or cannot be induced by heat or light. We think that tributylstannyl radicals are likely to be generated by a preliminary oxidation step of the thiol, producing intermediate thiyl radicals and disulfide. The oxidation process should be favoured by the acidity of the thiophenol [6].

$$ArSH \rightleftharpoons ArS^- + H^+$$

$$ArS^- + O_2 \rightarrow ArS^{\cdot} + O_2^{\cdot-}$$

$$ArS^- + O_2^{\cdot-} \rightarrow ArS^{\cdot} + O_2$$

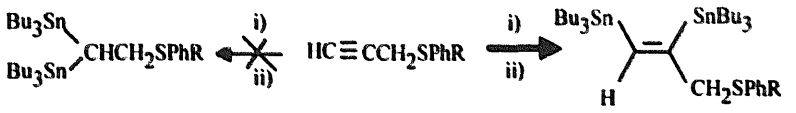
$$2\,ArS^{\cdot} \rightleftharpoons ArSSAr$$

$$ArS^{\cdot} + Bu_3SnH \rightleftharpoons Bu_3Sn^{\cdot} + ArSH$$

Such a behaviour could account for the radicalar

Table 1
Elemental analysis and yields

	Bi-metallic compounds	Yields %	Analysis found (calcd.)%
(1)	$[Bu_3Sn]_2CHCH_2Ph$	89	C: 56.28 (56.17); H: 9.30 (9.13); Sn: 34.48 (34.70)
(2)	$[Bu_3Sn]_2CHCH_2(CH_2)_4CH_3$	65	C: 55.36 (55.52); H: 9.99 (10.19); Sn: 34.19 (34.29)
(3)	$[Bu_3Sn]_2CHCH_2CH_2NHPh$	51	C: 55.69 (55.57); H: 9.18 (9.19); Sn: 32.60 (33.28)
(4)	$[Bu_3Sn]_2CHCH_2CH_2OPh$	73	C: 55.38 (55.49); H: 8.80 (9.03); Sn: 33.09 (33.24)
(5)	$[Bu_3Sn]_2CHCH_2CH_2OTHP$	79	C: 53.25 (53.21); H: 9.74 (9.49); O: 4.59 (4.43); Sn: 33.18 (32.87)
(6)	$[Bu_3Sn]_2CHCH_2CH[CH_3]OTHP$	27	C: 53.99 (53.83); H: 9.90 (9.58); Sn: 31.97 (32.24)
(7)	$[Bu_3Sn]_2CHCH_2CO_2CH_3$ [14]	92	C: 50.47 (50.48); H: 9.08 (9.08); O: 4.24 (4.80); Sn: 35.56 (35.64)
(8)	$[Bu_3Sn]_2CHCH_2CH_2OH$	80	C: 50.92 (50.82); H: 9.42 (9.47); Sn: 36.97 (37.20)
(9)	$[Bu_3Sn]_2CHCH_2CH[CH_3]OH$	35	C: 51.54 (51.56); H: 9.56 (9.58); O: 2.68 (2.45); Sn: 36.16 (36.40)
(10)	$[Bu_3Sn]_2CHCH_2CH_2CH_2OH$	75	C: 51.22 (51.57); H: 9.39 (9.58); O: 2.67 (2.45); Sn: 37.62 (36.40)
(11)	$[Bu_3Sn]_2CHCH_2CH_2CH_2SPh$	69	C: 54.97 (54.86); H: 8.81 (8.94); Sn: 31.04 (31.90)
(12)	$[Bu_3Sn]_2CHCH_2CH_2OPhpCH_3$	75	C: 56.27 (56.07); H: 8.93 (9.13); Sn: 32.03 (32.60)
(13)	$[Bu_3Sn]_2CHCH_2CH_2CH[CH_3]OH$	40	C: 52.18 (52.28); H: 9.28 (9.68); O: 2.33 (2.40); Sn: 36.35 (35.63)
(14)	$Bu_3SnCH{=}C[SnBu_3]CH_2OPh$	15	C: 55.99 (55.65); H: 8.81 (8.77); Sn: 31.46 (33.33)
(15)	$Bu_3SnCH{=}C[SnBu_3]CH_2SPh$	80	C: 54.09 (54.42); H: 8.63 (8.58); Sn: 31.46 (32.60)



R = H, CH_3

i) 2.5 eq. Bu_3SnH; ii) 0.1 to 1 eq. *p*-CH_3PhSH or *p*-CH_3OPhSH, ambient temperature.

Scheme 2.

initiation of both double stannylation and hydrostannation reactions *at ambient temperature in the absence of standard initiators* and explain the failure of alkylthiol-catalyzed double stannylation and double hydrostannation attempts. GC-MS analyses of commercially available thiols confirm the presence of traces of corresponding disulfides (< 5%).

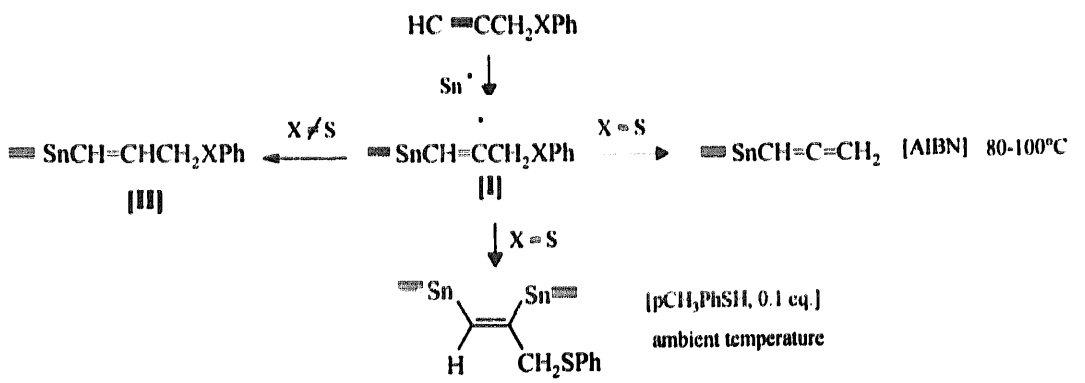
Let us first consider the double stannylation pathway. Keeping in mind that propargyl sulfides HC ≡ CCH_2SPhR (R = Ph,CH_3) cannot lead to double hydrostannation adducts whatever the experimental conditions and that the presence of an adjacent aryl ring to the sulfur atom is essential for the double stannylation process, it is reasonable to think that the formation of these adducts results from a favoured addition of the further stannyl radical on the β-vinylstannyl radical intermediate **[I]** rather than resulting from a competing hydrogen atom transfer from stannane leading to **[II]** (Scheme 3). In addition, while the fragmentation reaction of **[I]** to stannylallene and thiyl radicals proved to be strongly favored in the presence of AIBN at high temperature (80–100°C), the stannylallene is not formed in our experimental conditions in the presence of small amounts of arylthiol *at ambient temperature*.

Hence, the β-vinylstannyl radical **[I]** might be stabilized by a 5-membered cyclisation on the adjacent phenyl ring **[I]** → **[IIII]** before formation of the normal addition product **[III]** (Scheme 4). Interactions between low-energy d-orbitals of the sulfur atom and the odd electron orbital might lead to interactions moving the phenyl ring and the C-centered radical together in view of cyclisation [3]. Alternative cyclisations of β-stannylvinyl radical on the adjacent sulfur atom leading to a strained sulfuranyl radical [7], as well as 4-membered cyclisations leading to a non-stabilized radical intermediate might be rejected.

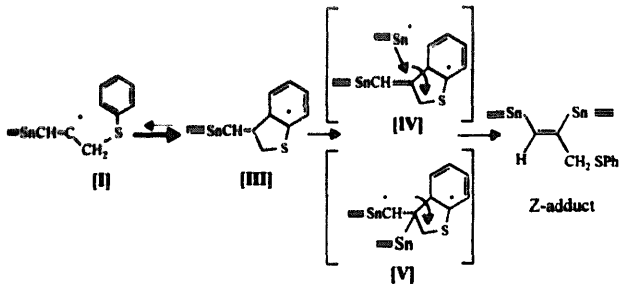
Two reaction pathways could be envisaged to account for the formation of a double stannylation adduct. Addition of the second equivalent of stannane could be interpreted either in terms of a concerted addition of the stannyl radical on the intermediate 5-membered stabilized radical **[III]** with concomitant rearomatization (**III** → **IV**) or in terms of the formation of a bi-radical intermediate (**III** → **V**) with subsequent rearomatization. Intermediate **[IV]** which entails less steric hindrance between the approaching stannyl group and the aromatic ring appears more consistent with the observed stereospecific formation of [Z]-adducts than intermediate **[V]** which should give rise to mixtures of stereoisomers. Such proposal requires that the equilibrium between species **[I]** and **[III]** should be displaced to **[IIII]** before the occurrence of the standard hydrogen abstraction reaction and the formation of **[III]**.

Before going further into the double stannylation mechanism and in order to get more information, let us now consider the double hydrostannation pathway. To delimit the role of the arylthiol in these reactions, some exploratory experiments have been carried out on phenyl acetylene and methyl propiolate (Scheme 5).

Attempts to achieve addition of stannane via two standard separate addition steps in the presence of AIBN failed. While the use of radical initiators such as AIBN instead of arylthiol affords in our experimental conditions only the monohydrostannylated α and β species, the desired double hydrostannation products were obtained immediately in the presence of a further equiva-



Scheme 3.



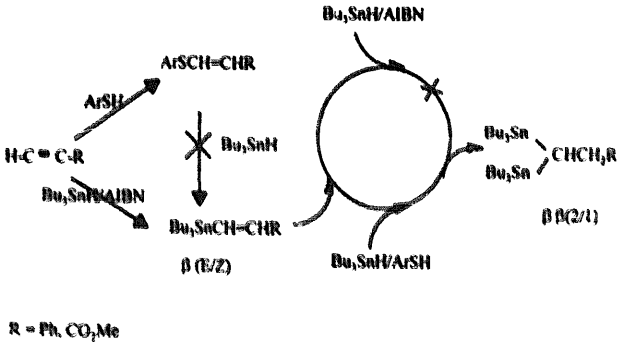
Scheme 4.

lent of thiol. On the other hand, no reaction could be observed by desulphurative stannylation of a conceivable intermediate vinylsulphide [8].

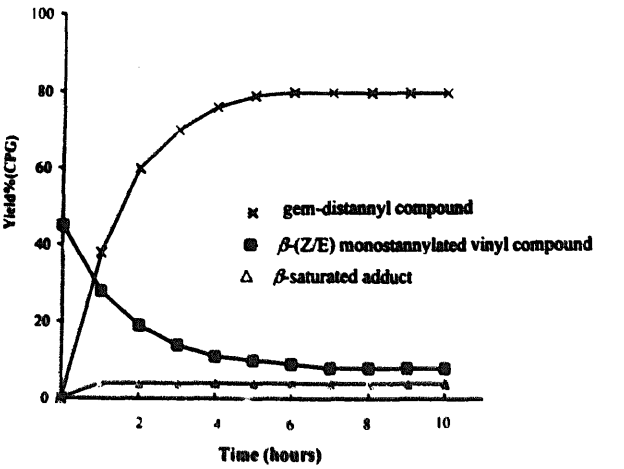
As expected, disappearance as function of time of initial $\beta-(Z/E)$ monostannylated vinyl compounds can be related to concomitant formation of gem-distannyl adducts. The conversion of the vinylstannane into 1,1-bis(tributylstannyl)-1-alkanes proved very straightforward. Double hydrostannation of methyl propiolate serves as a typical example (Scheme 6).

$$\underset{1\,eq.}{HC{\equiv}CCO_2Me} + \underset{2.5\,eq.}{Bu_3SnH} + \underset{1\,eq.}{pCH_3OPhSH} \rightarrow (Bu_3Sn)_2CHCH_2CO_2Me.$$

GC monitoring of the hydrostannation reaction of methyl propiolate *at ambient temperature* and in the presence of one equivalent of thiol displays the vinylstannane consumption with time, together with the formation of a β-saturated adduct, whose concentration appears to be time independent in the course of the reaction. The diagram indicates total vinylstannane consumption after 5 h. In addition, the reaction produces stannylthiolates of the type $Bu_3SnSPhOCH_3$ as by-products arising from a competing reaction between the thiol and the stannane [9]. Concentration time dependence of the stannylthiolate is not displayed on the diagram because of low resolution of the signals in the chromatographic conditions. Stannylthiolate does not operate in the mechanistic pathway, as confirmed by the failure to isolate double hydrostannation and/or double stannylation adducts by its use instead of arylthiol.



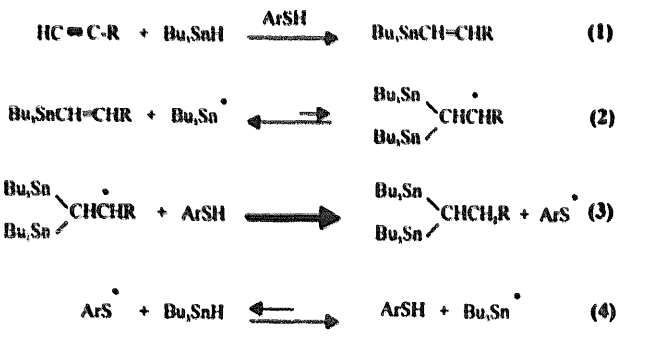
Scheme 5.



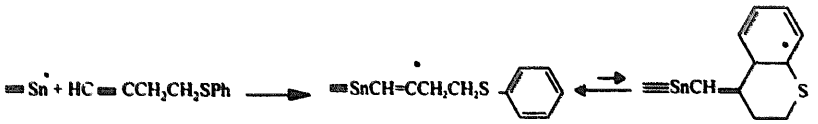
Scheme 6.

In view of the previously stated considerations about the preliminary oxidation step of the arylthiol to generate tributylstannyl radicals, the question which now arises is that of the role of the thiol in the addition step of the second equivalent of stannane onto the vinyltin intermediate. Evidence is presented to show that the important factor appears to be the stability of the intermediate radical of the type Sn_2CHCHR, which in the absence of thiol may lose a stannyl radical rather than abstracting a hydrogen atom from a further stannane molecule [10]. In contrast, in the presence of one equivalent of thiol the gem-bis(tributylstannyl) radical should be immediately trapped by the electrophilic hydrogen atom of the thiol at the expense of the nucleophilic one of the stannane. The probable reaction mechanism which accommodates the results better is shown as follows (Scheme 7):

Generated thiyl radicals (step 3) do react with tributylstannane in a propagation step 4. The observed polarity reversal catalysis mechanism assumes that reversible addition of a stannyl radical (step 2) leads to a nearly quantitative shift towards 1,1-distannyl radicals, the driving force of which being attributed to the relative rates of hydrogen atom transfer between stannane ($k_{25°C} = 2.4 \cdot 10^6\ M^{-1}\ s^{-1}$) [11] and thiol ($k_{25°C} = 1.4 \cdot$



Scheme 7.



Scheme 8.

10^8 M^{-1} s^{-1}) [12]. Such a mechanism is in agreement with Robert's observations that alkenes could be easily hydrosilylated in the presence of AIBN and thiol [13].

Confirmation of the radicalar character of the double hydrostannation process has been provided by addition of radical initiators/inhibitors. As expected, the reaction rates are increased by adding AIBN and decreased (in case of methyl propiolate) or suppressed entirely in the presence of TBE (tert-butylcatechol) in all other examples.

These results underline the catalytic efficiency of the tributylstannane/arylthiol system as radical initiator *at ambient temperature*. An example is given by the tributylstannane reduction of benzyl chloride which is known to react with difficulty compared with corresponding bromide and iodide. While benzyl chloride reduction has to be initiated with AIBN, UV as well as thermal initiation, the reaction can be achieved easily in the presence of ~ 5% arylthiol at ambient temperature with a 60% yield.

Since any mechanistic conclusion from the available data rely on characteristic evolution of a common β-stannylvinyl radical intermediate, i.e., either on the hypothesis of a 5-membered ring intermediate or on a competing hydrogen atom transfer from the stannane, it appears necessary to determine the behaviour of propargylic sulfides in which a preferentially stabilized 6-membered ring closure onto the adjacent phenyl ring could occur. 4-(phenylthio)but-1-yne serves as a typical example (Scheme 8):

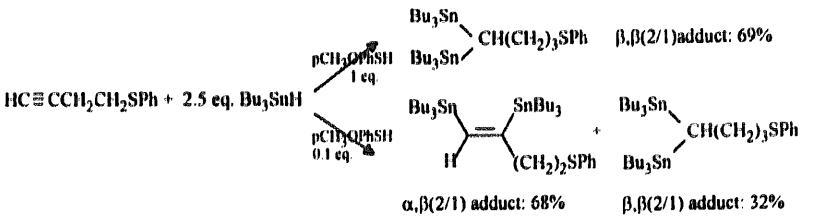
The behaviour of this compound has been studied both in the conditions of the double stannylation and double hydrostannation, that is at low and high thiol concentrations. At low thiol concentration one can expect to favour the standard hydrogen atom transfer reaction from the stannane (leading to the saturated gem-distannyl compound via intermediate [II]: (Schemes 3 and 7) at the expense of the cyclisation reaction because of rate competing between the less favourable 6-membered radical formation than the 5-membered one. Consequently, the reaction should afford a mixture of double stannylation and double hydrostannation adducts while at high concentrations the thiol plays the previously reported role of hydrogen atom donor, leading exclusively to the corresponding gem-distannyl adduct (Scheme 9).

In conclusion, the 5-membered cyclisation ring closure appears to play the fundamental role in orienting the stannane addition to alkynyl phenyl sulfides, the arylthiol acting as radical initiator *at the ambient temperature*. This behaviour contrasts with the reactivity of vinyl radicals that not bear a sulfur atom in the side chain where the arylthiol acts both as radical initiator *at the ambient temperature* and as polarity reversal catalyst for hydrogen atom transfer.

In this full account of our studies in the double stannylation and double hydrostannation area, we have established the optimum mechanistic and experimental conditions for a directed synthesis of dimetalated compounds which find increasing utility in organic synthesis [14].

3. Experimental

Starting materials were either commercial products or were prepared according to literature procedures. Double stannylation and double hydrostannation reactions were carried out in an argon atmosphere. ^{13}C and ^{119}Sn NMR spectra were obtained as described in earlier papers by us [1]. Combined gas chromatography-mass spectrometry was conducted with a Hewlett-Packard model 5890 instrument fitted with a Cpsil 5 capillary column, whereas gas chromatographic analyses were performed on a Varian 3400 using a DB5 capillary column. Mass spectra were obtained using a VG Auto Spec. Q. instrument. Elemental analysis were performed by the 'Service Central d'Analyses du CNRS' of Vernaison (Table 1).



Scheme 9.

3.1. General procedure for the double stannylation reaction: Synthesis of 1,2-bis(tributylstannyl)-1-alkenes

Tributylstannane [4] (7.3 g; 25 mmol) was added to a mixture of propargylic compound (10 mmol) in the presence of some cristals of parathiophenol ($\sim 10^{-3}$ mol). The mixture was stirred at ambient temperature for 48 h and then purified at ca. 10^{-4} mm Hg using a Kugelrohr apparatus.

3.2. General procedure for the double hydrostannation reaction: Synthesis of gem-bis(tributylstannyl)alkanes

Tributylstannane (2.18 g; 7.5 mmol) was added to 3 mmol of propargylic compound. Then, a solution of 0.42 g (3 mmol) of p-methoxythiophenol in 3 ml anhydrous THF was added to the mixture. After stirring 24 h at ambient temperature, the crude reaction product was purified as mentioned above.

2-Phenyl-1,1-bis(tributylstannyl)ethane (1)
^{119}Sn NMR (C_6D_6, δ ppm): + 7.70 [$^2J(^{119}SnC^{117}Sn)$ = 150.6 Hz].

1,1-Bis(tributylstannyl)octane (2)
^{119}Sn NMR (C_6D_6, δ ppm): + 8.76 [$^2J(^{119}SnC^{117}Sn)$ = 149.6 Hz].

3-N-Phenyl-1,1-bis(tributylstannyl)propane (3)
^{119}Sn NMR (C_6D_6, δ ppm): + 9.62 [$^2J(^{119}SnC^{117}Sn)$ = 158.8 Hz].

3-Phenoxy-1,1-bis(tributylstannyl)propane (4)
^{119}Sn NMR (C_6D_6, δ ppm): + 10.33 [$^2J(^{119}SnC^{117}Sn)$ = 159.1 Hz].

3-Tetrahydropyranyloxy-1,1-bis(tributylstannyl)propane (5)
^{119}Sn NMR (C_6D_6, δ ppm): + 10.32 [$^2J(^{119}SnC^{119}Sn)$ = 165.9 Hz, $^2J(^{119}SnC^{117}Sn)$ = 158.7 Hz]; + 11.55 [$^2J(^{119}SnC^{119}Sn)$ = 166.0 Hz, $^2J(^{119}SnC^{117}Sn)$ = 158.9 Hz].

3-Tetrahydropyranyloxy-1,1-bis(tributylstannyl)butane (6)
^{119}Sn NMR (C_6D_6, δ ppm): *Diastereoisomer A*: + 10.60 [$^2J(^{119}SnC^{119}Sn)$ = 173.7 Hz, $^2J(^{119}SnC^{117}Sn)$ = 166.1 Hz]; + 11.52 [$^2J(^{119}SnC^{119}Sn)$ = 173.8 Hz, $^2J(^{119}SnC^{117}Sn)$ = 166.0 Hz]; *Diastereoisomer B*: + 10.97 [$^2J(^{119}SnC^{119}Sn)$ = 175.9 Hz, $^2J(^{119}SnC^{117}Sn)$ = 168.2 Hz]; + 11.21 [$^2J(^{119}SnC^{119}Sn)$ = 176.0 Hz, $^2J(^{119}SnC^{117}Sn)$ = 168.1 Hz].

Methyl-3,3-bis(tributylstannyl)propionate [15] *(7)*
^{119}Sn NMR (C_6D_6, δ ppm): + 11.12 [$^2J(^{119}SnC^{117}Sn)$ = 153.7 Hz].

3,3-Bis(tributylstannyl)propanol (8)
^{119}Sn NMR (C_6D_6, δ ppm): + 10.30 [$^2J(^{119}SnC^{117}Sn)$ = 159.8 Hz].

4,4-Bis(tributylstannyl)butan-2-ol [16] *(9)*
^{119}Sn NMR (C_6D_6, δ ppm): + 9.22 [$^2J(^{119}SnC^{119}Sn)$ = 168.3 Hz, $^2J(^{119}SnC^{117}Sn)$ = 160.8 Hz]; + 10.27 [$^2J(^{119}SnC^{119}Sn)$ = 168.5 Hz, $^2J(^{119}SnC^{117}Sn)$ = 161.0 Hz].

4,4-Bis(tributylstannyl)butanol (10)
^{119}Sn NMR (C_6D_6, δ ppm): + 8.93 [$^2J(^{119}SnC^{117}Sn)$ = 152.7 Hz].

4-Phenylthio-1,1-bis(tributylstannyl)-butane (11)
^{119}Sn NMR (C_6D_6, δ ppm): + 9.24 [$^2J(^{119}SnC^{117}Sn)$ = 154.8 Hz].

3-p-Tolyloxy-1,1-bis(tributylstannyl)propane (12)
^{119}Sn NMR (C_6D_6, δ ppm): + 10.34 [$^2J(^{119}SnC^{117}Sn)$ = 158.5 Hz].

5,5-Bis(tributylstannyl)pentan-2-ol (13)
^{119}Sn NMR (C_6D_6, δ ppm): + 8.91 [$^2J(^{119}SnC^{119}Sn)$ = 168.3 Hz, $^2J(^{119}SnC^{117}Sn)$ = 151.3 Hz]; + 9.12 [$^2J(^{119}SnC^{119}Sn)$ = 168.5 Hz, $^2J(^{119}SnC^{117}Sn)$ = 151.2 Hz].

(Z)-3-Phenoxy-1,2-bis(tributylstannyl)prop-1-ene (14)
^{119}Sn NMR (C_6D_6, δ ppm): −55.06 [$^3J(^{119}Sn-^{119}Sn)$ = 268.4 Hz, $^3J(^{119}Sn-^{117}Sn)$ = 256.5 Hz]; −65.74 [$^3J(^{119}Sn-^{119}Sn)$ = 268.2 Hz, $^3J(^{119}Sn-^{117}Sn)$ = 256.3 Hz].

(Z)-3-Phenylthio-1,2-bis(tributylstannyl)prop-1-ene (15)
^{119}Sn NMR (C_6D_6, δ ppm): −54.30 [$^3J(^{119}Sn-^{119}Sn)$ = 266.1 Hz, $^3J(^{119}Sn-^{117}Sn)$ = 254.3 Hz]; −66.06 [$^3J(^{119}Sn-^{119}Sn)$ = 266.0 Hz, $^3J(^{119}Sn-^{117}Sn)$ = 254.2 Hz].

(Z)-4-Phenylthio-1,2-bis(tributylstannyl)but-1-ene **{$Bu_3SnCH=C[SnBu_3](CH_2)_2SPh$}**
^{119}Sn NMR (C_6D_6, δ ppm): −54.44 [$^3J(^{119}Sn-^{119}Sn)$ = 298.9 Hz, $^3J(^{119}Sn-^{117}Sn)$ = 286.2 Hz]; −67.35 [$^3J(^{119}Sn-^{119}Sn)$ = 298.9 Hz, $^3J(^{119}Sn-^{117}Sn)$ = 285.1 Hz].

(Z)-3-(N-Phenylamino)-1,2-bis(tributylstannyl)prop-1-ene **{$Bu_3SnCH=C[SnBu_3]CH_2NHPh$}**
^{119}Sn NMR (C_6D_6, δ ppm): −56.00 [$^3J(^{119}Sn-^{119}Sn)$ = 288.5 Hz, $^3J(^{119}Sn-^{117}Sn)$ = 275.6 Hz]; −65.63 [$^3J(^{119}Sn-^{119}Sn)$ = 288.8 Hz, $^3J(^{119}Sn-^{117}Sn)$ = 276.3 Hz].

1-(p-Methoxyphenyl)-3,3-bis(tributylstannyl)propanol **{$[Bu_3Sn]_2CHCH_2CH(OH)Ph_pOMe$}**
^{119}Sn NMR ($CDCl_3$, δ ppm): + 7.95/ + 9.10.

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