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Synthesis, characterisation and reactivity of 2-functionalised vinylstannanes

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Abstract

The functionalised vinylstannanes of the type (*E*)/(*Z*)-Ph_3SnCR'=$CHYR_n$ and (*E*)/(*Z*)-$Ph_3SnC(YR_n)$=CHR' ($YR_n = NMe_2$, OEt, SMe, SEt; $R' = Ph$, Bu (*n*-butyl), Pe (*n*-pentyl), H) were prepared by non-catalysed or Pd-catalysed hydrostannylation reactions. Particular stereoisomers were isolated by means of preparative HPLC and fully characterised using ^1H-, ^{13}C- and ^{119}Sn-NMR spectroscopy. The reactions of 2-functionalised vinylstannanes (*E*)/(*Z*)-Ph_3SnCR'=$CHYR_n$ with acetic and chloroacetic acid in $CDCl_3$ proceeded by protodestannylation yielding $Ph_3SnOOCCH_2X$ (X = H, Cl) and CHR'=$CHYR_n$. The results of kinetics measurements reveal that Lewis-basic substituents YR_n facilitate the electrophilic cleavage of Sn–C= bonds, and this effect increases with the basicity of the heteroatom Y, i.e. in the order S < O < N. In contrast, an alkyl substituent at the α-carbon atom slightly suppresses the reaction rate. Furthermore it was found that the *E*-isomers react faster than the corresponding *Z*-isomers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Functionalised vinylstannanes; Hydrostannylation; Protodestannylation; NMR; Kinetics

1. Introduction

Organometallics containing not only M–C bonds as reactive sites but also other centres of high reactivity represent a very interesting field of organometallic chemistry. Introduction of a heteroatom Y (Y Group 14–17 element) into an organoligand can have a profound influence on the structure, stability and reactivity of organometallic compounds and consequently open the possibility of entirely new reactions [1].

For example, organometallic compounds with Lewis-basic 2-functionalised ethyl ligands L_xM–CH_2–CH_2–YR_n ($YR_n = NR_2$, OR, Cl,...; R = alkyl, aryl, H) can undergo elimination reaction, so-called heterolytic fragmentation [2], either spontaneously (M = Li or Mg) [3] or after reaction with a suitable electrophile (Scheme 1) [4]. However, there are only a few reports on analogous 2-functionalised vinylmetallic compounds L_xM–CH=CH–YR_n, and the observations of heterolytic fragmentation at this type of compound are quite rare and partially ambiguous.

This work therefore deals with the preparation, characterisation and reactivity of 2-functionalised vinylstannanes of the type Ph_3SnCR'=$CHYR_n$ ($YR_n = NMe_2$, OEt, SMe, SEt; $R' = Ph$, Bu (*n*-butyl), Pe (*n*-pentyl), H). The aim is to elucidate relationships between the type of the Lewis-basic substituent and stereoisomerism on the one hand and reactivity on the other hand.

2. Results and discussion

2.1. Synthesis

The functionalised vinyltin compounds were prepared by either non-catalysed or Pd-catalysed hydrostannylation of functionalised alkynes **1**–**5** with triphenyltin hydride which proceeds according to Scheme 2. Selectivities of particular reactions determined by means of ^1H- and/or ^{119}Sn-NMR spectroscopy of crude reaction mixtures are summarised in Tables 1 and 2.

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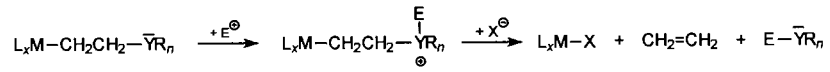
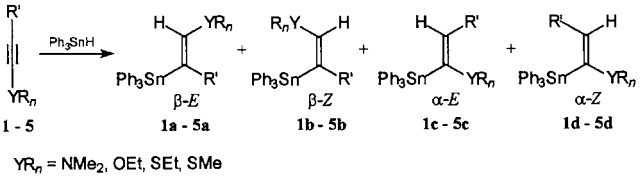


Scheme 1.



Scheme 2.

Non-catalysed hydrostannylations were carried out in hexane at elevated temperature (50–55°C). No radical initiator was used because a slightly elevated temperature is sufficient to induce homolytic cleavage of the Sn–H bond and initiation of the radical reaction. The Pd-catalysed hydrostannylation ([$Pd(PPh_3)_4$]) was performed in THF at −30°C in order to suppress radical reaction of Ph_3SnH. In all cases, non-catalysed hydrostannylation as well as Pd-catalysed hydrostannylation provided vinyltin compounds in yields of about 90% or higher along with a negligibly small amount of hexaphenyldistannane and other minor side products.

Non-catalysed hydrostannylations afforded the desired β-*Z*-isomers with quite high stereo- and regioselectivity. There is an exception for HC≡CSEt (**4**) (Table 1, entry 4) which could be caused either by a higher rate of isomerisation or by a small excess of organotin hydride arising due to lability of the alkyne [5]. Furthermore, slightly lower regioselectivity was observed in the case of BuC≡COEt (**3**) (Table 1, entry 3) where about 20% of α-isomers were formed. For the non-catalysed reaction of triphenyltinhydride with PeC≡CSMe (**5**) (Table 1, entry 5) selectivity could not be determined exactly because it was impossible to identify unambiguously minor products.

Pd-catalysed hydrostannylation, being a stereoselective *cis*-addition, was used for preparation of *E*-isomers [6]. However, the reactions of thioalkynes **4** and **5** provided the α-*E*-isomers **4c** and **5c** (Table 2, entries 3 and 4) selectively, as was already shown for R′/YR_n=Ph/SMe [7]. On the other hand, Pd-catalysed hydrostannylation of alkoxyalkynes **2** and **3** (Table 2, entries 1 and 2) afforded the desired β-*E*-isomers **2a** and **3a** but with low regioselectivity.

Table 2
Selectivity of Pd-catalysed hydrostannylation

Entry	Alkyne			Selectivity (%)	
		R′	YR_n	β-*E* (**a**)	α-*E* (**c**)
1	**2**	H	OEt	70	30
2	**3**	Bu	OEt	46	54
3	**4**	H	SEt	0	100
4	**5**	Pe	SMe	0	100

Except for (*E*)-Ph_3SnCH=CHSEt (**4a**), standard work-up procedures did not give β-functionalised vinylstannanes in the isomerically pure state. Therefore, the desired stereoisomers (*E*)- and (*Z*)-Ph_3SnCH=CHOEt (**2a**/**2b**), (*E*)- and (*Z*)-$Ph_3SnC(Bu)$=CHOEt (**3a**/**3b**), (*Z*)-Ph_3SnCH=CHSEt (**4b**) were isolated from crude reaction mixtures by means of preparative HPLC using direct phase (silicagel, hexane:THF = 100:6). For (*Z*)-$Ph_3SnC(Ph)$=$CHNMe_2$ (**1b**) [7] and (*Z*)-Ph_3Sn-C(Pe)=CHSMe (**5b**) the selectivity of hydrostannylation was relatively high, and these compounds were used without further purification.

2.2. Characterisation

Except for (*Z*)-$Ph_3SnC(Ph)$=$CHNMe_2$ (**1b**) [7], ^{1}H-NMR parameters of vinylic protons, summarised in Table 3, enable one to distinguish between particular isomers and to identify them unambiguously even in

Table 1
Selectivity of non-catalysed hydrostannylation

Entry	Alkyne			Selectivity (%)			
		R′	YR_n	β-*E* (**a**)	β-*Z* (**b**)	α-*E* (**c**)	α-*Z* (**d**)
1	**1** [a]	Ph	NMe_2	0	100	0	0
2	**2**	H	OEt	12	88	0	
3	**3**	Bu	OEt	0	80	3	17
4	**4**	H	SEt	81	19	0	
5	**5**	Pe	SMe	[b]	≥92	[b]	[b]

[a] Ref. [7].
[b] Not unambiguously spectroscopically proved.

complex mixtures. The data of **1b** are given in Ref. [7]. The values of ^{1}H chemical shifts lie in a very wide region (δ^1H 4.2–7.4) and they are strongly dependent on the heteroatom Y, and on the configuration of substituents on the vinylic group.

For functionalised vinylstannanes with two vinylic protons (R′ = H) there are three possible isomers (β-*Z*, β-*E* and α). The β-isomers have vinylic protons in vicinal positions. In the case of the β-*E* isomers **2a** and **4a**, the vinylic protons are mutually in *trans*-positions and the corresponding coupling constants $^3J(^1H,^1H)$ are 15.6 and 18.4 Hz, respectively. On the contrary, in the case of β-*Z* isomers **2b** and **4b**, the vinylic protons are in mutual *cis*-positions and the $^3J(^1H,^1H)$ coupling constants are roughly two times smaller (6.8 Hz **2b**, 11.3 Hz **4b**). The α-isomers **2c** and **4c** have vinylic protons in geminal position, and thus the coupling constants $^2J(^1H,^1H)$ are usually less than 2 Hz [8]. The assignment of both vinylic proton resonances was done on the basis of the relationship between relevant $J(^{119}Sn,^1H)$ coupling constants. The coupling constants $^2J(^{119}Sn,^1H_{gem})$ are slightly larger than $^3J(^{119}Sn,^1H_{cis})$ while $^3J(^{119}Sn,^1H_{trans})$ are about two times larger than $^3J(^{119}Sn,^1H_{cis})$ [9]. In the cases of β-*E*-isomers, the values of both coupling constants $^2J(^{119}Sn,^1H_{gem})$ and $^3J(^{119}Sn,^1H_{cis})$ are very similar. The assignment was confirmed by the evaluation of ^{1}H chemical shifts: resonances of protons in vicinal position (SnCH=C*H*) are shifted significantly downfield with respect to the resonances of protons in geminal position (SnC*H*=CH).

Functionalised vinylstannanes with one vinylic proton (R′ = alkyl) form four isomers (β-*E*, β-*Z*, α-*E* and α-*Z*). The $^3J(^{119}Sn,^1H)$ coupling constants enable one to distinguish between stereoisomers because this parameter predicts the mutual positions of the tin and the hydrogen atom at the C=C bond (see above). The magnitude of $^3J(^{119}Sn,^1H)$ in the range of 30–70 Hz indicates the mutual *cis* positions of the Ph_3Sn substituent and vinylic proton (*E*-isomers), and in the range of 120–160 Hz the mutual *trans* positions (*Z*-isomers). Constitutional isomers can be distinguished using the spectral pattern of the vinylic proton. In the case of α-isomers, the signal of the vinylic proton reveals coupling with protons on the α-carbon atom of alkyl substituent R′. The appropriate coupling constants $^3J(^1H,^1H)$ are within the range 6.8–7.6 Hz. On the other hand, vinylic protons of β-isomers give rise to singlet signals in ^{1}H-NMR spectra. In particular cases of well resolved spectra, triplets can be observed but the corresponding coupling constant $^4J(^1H,^1H)$ is less than 1 Hz.

In the case of (*Z*)-$Ph_3SnC(Ph)$=$CHNMe_2$ (**1b**), it was impossible to distinguish between α- and β-isomers by means of conventional ^{1}H-NMR experiment because the signal of the vinylic proton is singlet in both cases. Therefore, **1b** was fully identified by means of $^1J(^{13}C,^{13}C)$ obtained using the 1D INADEQUATE technique [7].

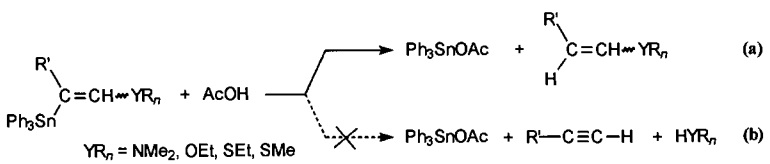
2.3. Reactions of 2-functionalised vinylstannanes with acids

2-Functionalised vinylstannanes (*E*)/(*Z*)-$Ph_3SnC(R')$=$CHYR_n$ (R′/YR_n=Ph/NMe_2 **1b**, H/OEt **2a**/**2b**, Bu/OEt **3a**/**3b**, H/SEt **4a**/**4b** and Pe/SMe **5b**) were treated with about two equivalents of acetic acid in $CDCl_3$ at room temperature. In all cases, protodestannylation reactions took place and vinylic

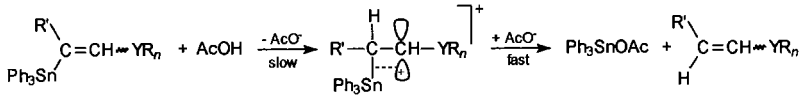
Table 3
^{1}H chemical shifts in ppm and relevant coupling constants in Hz of vinylic protons of functionalised vinylstannanes

Compound	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**3d**	**4a**	**4b**	**4c**	**5b**	**5c**
$\delta(^1H_{gem})$	4.92	4.88						6.21	6.38			
$J(^{119}Sn,^1H_{gem})$	52.0	62.2						75.0	73.9			
$\delta(^1H_{cis})$	6.43		4.27	5.93		4.90		6.67		5.40		5.88
$^3J(^{119}Sn,^1H_{cis})$	42.8		41.6	42.0		34.5		75.1		71.7		67.5
$\delta(^1H_{trans})$		6.94	4.87		6.68		5.50		7.34	5.69	6.78	
$^3J(^{119}Sn,^1H_{trans})$		127.7	130.3		122.7		126.9		167.7	148.6	151.3	
$J(^1H,^1H)$	15.6	6.8	1.5			7.0	7.6	18.4	11.3	[a]		6.8
Multiplicities	d	d	d	s	s	t	t	d	d	d	s	t

[a] Not resolved.



Scheme 3.



Scheme 4.

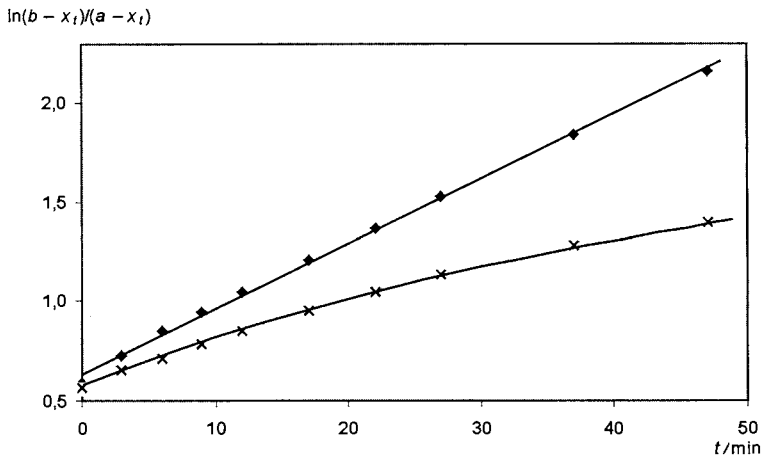


Fig. 1. Verification of second-order kinetics derived from the decrease in the organotin substrate **2a** (◆) and increase in product CH_2=CHOEt (×) for the reaction of **2a** with acetic acid in $CDCl_3$.

substituents were cleaved selectively (Scheme 3a). No evidence of heterolytic fragmentation (Scheme 3b) or other side reactions was obtained.

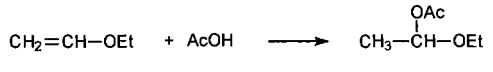
(*Z*)-$Ph_3SnC(Ph)$=$CHNMe_2$ (**1b**) reacted with acetic acid very readily, and the selective cleavage of the 2-aminofunctionalised vinyl group (Scheme 3a) was complete within 5 min. Moreover, it was found that **1b** is even moisture sensitive because water as weak acid cleaves the tin–vinyl bond affording Ph_3SnOH and (*E*)-2-(*N*,*N*-dimethylamino)phenylethene.

On the other hand, for (*Z*)-$Ph_3SnC(Pe)$=CHSMe (**5b**) a very slow reaction was observed. Therefore stronger chloroacetic acid was used instead of acetic acid. Then protodestannylation was significantly faster and about 50% of organotin substrate **5b** was converted within 20 h. However, this reaction afforded likewise about 30% of $Ph_2Sn(OOCCH_2Cl)_2$ and benzene which denoted that the phenyl group was also cleaved off. Furthermore less then 5% of 1-heptyne was formed. Thus, it might be supposed that the heterolytic fragmentation proceeded as a minor side reaction. However, the third product of prospective heterolytic fragmentation, i.e. methyl mercaptane, was not found in the reaction mixture. Moreover, since **5b** was used as a raw product of hydrostannylation with purity of 92% the source of alkyne might be an impurity.

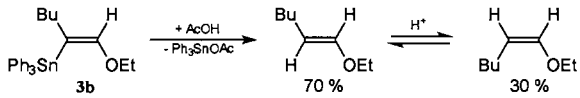
For comparison, the reactions of Ph_3SnCH=CH_2 (**6**) with acids were also investigated. When **6** was treated with acetic acid (molar ratio 1:2) in $CDCl_3$ at room temperature no reaction was observed within one month. The reaction of Ph_3SnCH=CH_2 with chloroacetic acid (molar ratio 1:5) under the same conditions was found to be rather slow and complex. After 2 days about 30% of starting triphenylvinylstannane remained unreacted. Furthermore it was proved that the reaction mixture contained a significant amount of benzene indicating that phenyl groups were cleaved. The ^{119}Sn-NMR spectrum showed that the reaction provided four organotin compounds ($\delta(^{119}Sn) = -279.1$ ppm/18%, -284.3 ppm/49%, -290.9 ppm/28%, -390.5 ppm/5%). Thus, it seems that phenyl and vinyl groups were cleaved simultaneously.

For the remaining six analogous 2-functionalised vinylstannanes (*E*)/(*Z*)-$Ph_3SnC(R')$=$CHYR_n$ (R'/YR_n = H/OEt **2a**/**2b**, Bu/OEt **3a**/**3b**, H/SEt **4a**/**4b**) reaction rates of prodestannylation (Scheme 3a) were between those two limits mentioned above. Thus, it was possible to follow the courses of reactions by ^{1}H-NMR spectroscopy and evaluate kinetics. In all cases, the rate of disappearance of the organotin substrate was found to be strictly second-order, in accordance with the suggested mechanism (Scheme 4) which is consistent with the general mechanism of electrophilic cleavage of the metal–vinyl bond [10]. However, the rates of product formation revealed considerable deviations from second-order kinetics as shown in Fig. 1 with **2a** as example.

Separate ^{1}H-NMR spectroscopic investigations showed that the primary products of protodestannylation CHR'=$CHYR_n$ (Scheme 3a) can undergo subsequent reactions. Namely, ethyl vinyl ether (formed in the reaction of **2a**/**2b** with AcOH) reacts with acetic acid under the same reaction conditions yielding 1-



Scheme 5.

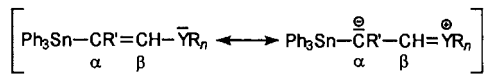


Scheme 6.

ethoxyethyl acetate (Scheme 5). Furthermore it was found that (*E*)-1-ethoxyhex-1-ene (formed in the reaction of **3b** with AcOH) most likely undergoes acid catalysed *E*/*Z*-isomerisation under the reaction conditions (Scheme 6). Probably, these slow subsequent reactions cause the deviations from second-order kinetics observed for product formations. In order to simplify evaluation of the kinetics, the subsequent reactions were neglected and the second-order rate constants were derived only from the decay of starting vinylstannanes which were practically unaffected because acetic acid was used in sufficient excess.

The values of second-order rate constants for particular 2-functionalised vinylstannanes summarised in Table 4 indicate three general effects.

1. Lewis-basicity of substituent YR_n. It seems obvious from mutual comparison of 2-functionalised vinylstannanes $Ph_3SnCR'=CHYR_n$ (**1b**–**5b**) with the corresponding non-functionalised triphenylvinylstannane $Ph_3SnCH=CH_2$ (**6**) that Lewis-basic substituents in β-position with respect to the tin atom facilitate electrophilic cleavage of the vinyl group. Moreover, a comparison of 2-thio-, 2-alkoxy- and 2-aminovinylstannanes reveals that the effect of Lewis-basic heteroatom increases with its basicity, i.e. in the sequence S < O < N.
2. Stereochemistry (*E*- versus *Z*-isomers). In all cases,



Scheme 7.

the differences in reactivity of stereoisomers are evident. *E*-isomers **2a** and **4a** react roughly ten times faster than the corresponding *Z*-isomers **2b** and **4b**, respectively. The compounds **3a** and **3b** containing a butyl substituent at the α-carbon atom reveal even greater diversity in the reaction rate: the *E*-isomer **3a** reacts more than fifty times faster than the *Z*-isomer **3b**.

3. α-Substituent. The comparison of **2a**, **2b** and **4b** on the one hand and **3a**, **3b** and **5b**, respectively, on the other hand shows that compounds with a butyl substituent at the α-carbon atom react slower than compounds without this substituent. The effect of the butyl substituent seems to be significantly stronger in the case of *Z*-isomers (**2b** and **3b**) which differ in reaction rate approximately eighteen times, while *E*-isomers (**2a** and **3a**) differ in reaction rate only about three times.

2.4. Discussion

In the accepted mechanism of protodestannylation of vinylstannanes (Scheme 4) the electrophile attacks the α-carbon atom yielding a carbocationic intermediate stabilised by hyperconjugation. Then the rapid attack of the nucleophile at the tin atom and subsequent splitting of the tin–carbon bond finishes the reaction [10]. Considering this mechanism the electronic influence of Lewis-basic substituents YR_n on the β-vinylic carbon atom can be discussed in the following way.

1. The interaction of the Lewis-basic substituent YR_n with the vinylic π bond results in an increase of

Table 4
Second-order rate constants of protodestannylation reactions, NBO charges and ^{13}C chemical shifts of the α-carbon atom of 2-functionaliased vinylstannanes

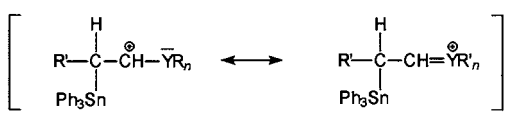
	R′	YR_n	Isomer	$\overline{k}$ (l mol^{-1} min^{-1})	$\delta(^{13}C^{\alpha})$ (ppm)	NBO charges [a]		
						C^{α}	C^{β}	Y
1b	Ph	NMe_2	*Z*	>1 [a]	113.53	[b]	[b]	[b]
2a	H	OEt	*E*	4.10×10^{-1}	88.97	−0.59	+0.10	−0.20
2b	H	OEt	*Z*	4.39×10^{-2}	94.92	−0.58	+0.10	−0.22
3a	Bu	OEt	*E*	1.27×10^{-1}	112.73	−0.53	+0.07	−0.22
3b	Bu	OEt	*Z*	2.35×10^{-3}	114.79	−0.53	+0.08	−0.19
4a	H	SEt	*E*	6.54×10^{-3}	117.61	−0.47	−0.16	+0.05
4b	H	SEt	*Z*	6.29×10^{-4}	126.19	−0.47	−0.16	+0.03
5b	Pe	SMe	*Z*	$<10^{-4}$ [a]	148.47	[b]	[b]	[b]
6	H	H		$\ll10^{-5}$ [a]	134.92	−0.49	−0.06	

[a] Estimated.
[b] Not calculated.

negative charges at the α-vinylic C atom (Scheme 7) which facilitates the rate-determining step of protodestannylation (Scheme 4). Regarding the electronegativity of the heteroatom Y and the preference for π conjugation for first-row elements over second-row elements, the expected order is S < O < N. For 2-ethoxy and 2-thiofunctionalised vinylstannanes it is fully in agreement with the values of rate constants, NBO charges [11] and ^{13}C chemical shifts of α-carbon functionalised vinylstannane atoms listed in Table 4.

2. The carbocationic intermediate (Scheme 4) is strongly stabilised by a Lewis-basic substituent YR_n through a π-type interaction (Scheme 8). The expected order is O < S ≪ N [12]. Thus, this seems to be the reason for the significantly faster reaction of 2-aminofunctionalised vinylstannane **1b** with acids in comparison with ethoxy- and thio-functionalised derivatives. Analogously, the stability of the non-functionalised triphenylvinylstannane **6** under the same reaction conditions in spite of the relatively low charge on the α-carbon atom can be understood.
3. The higher reactivity of *E*-isomers over *Z*-isomers might be a consequence of intramolecular nucleophilic assistance Y → Sn, which can suppress the cleavage of the vinyl group in *Z*-isomers. An analogous phenomenon was found for halodestannylations of some vinylstannanes, which form five- or four-membered rings involving weak Y → Sn interaction [13]. This hypothesis is supported by the fact that an upfield shift of $\delta(^{119}Sn)$ by about 18 ppm is observed for *Z*-isomers with respect to *E*-isomers in all three pairs of 2-functionalised vinylstannanes **2a**/**2b**, **3a**/**3b** and **4a**/**4b**. However, this result is not conclusive because ^{119}Sn resonances are usually shifted by more than 60 ppm to upper field if an additional Y → Sn coordination exists [9].
4. The experimental findings that alkyl substituents on the α-vinylic C atom give rise to a slight decrease of reaction rate (cf. **3a**/**2a**, **3b**/**2b**, **5b**/**4b**) can be explained in terms of steric demand of these substituents.

Summarising, this paper shows that for 2-functionalised vinylstannanes an electrophile preferably attacks the α-carbon atom resulting in the cleavage of Sn–C= bonds (protodestannylation). Under normal circumstances this seems to be the preferred reaction pathway in comparison with electrophilic attack at the Lewis-basic heteroatom Y with subsequent heterolytic fragmentation reaction. Furthermore it was found that the substituents YR_n facilitate the rate of protodestannylation. The overall effect depends on the nature of the heteroatomic centre YR_n and its stereo-orientation with respect to the tin atom (*E*- versus *Z*-isomers).



Scheme 8.

3. Experimental

3.1. General

3.1.1. Instruments

Microanalyses (C, H, S) were carried out using a Fison EA 1108 instrument in the Microanalytical Laboratory at the University of Pardubice. ^1H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded using a 5 mm tuneable probe on a Bruker AMX 360 spectrometer in $CDCl_3$ at 300 K. Chemical shifts are given in parts per million with respect to Me_4Si [δ ^1H (HMDS) = 0.05; δ ^{13}C ($CDCl_3$) = 77.00] and Me_4Sn [δ $^{119}Sn = 0.0$ for Ξ (^{119}Sn) = 37.2906174 MHz] [14]. Preparative HPLC was performed on a Septech Merck apparatus equipped with UV detector (254 nm) using direct phase system–mobile phase *n*-hexane–THF (100:6); stationary phase Lichrosorb Silicagel 60 (7 μm); column length 25 cm; column diameter 2.5 cm. Gas samples were analysed using a Chrompack CP 9000 instrument equipped with capillary column (plot fused silica, Al_2O_3/KCl, length 50 m) and FID detector. Peaks were identified by means of reference substances.

3.1.2. Preparative techniques and starting materials

The reactions were carried out under argon using standard Schlenk techniques [15]. Hexane was dried with $LiAlH_4$. THF was distilled from sodium benzophenone ketyl. 1-Heptyne, dimethyldisulfide, *n*-butyllithium and ethoxyethyne **2** were commercially available. Except for **2**, which was distilled in vacuo at room temperature prior to use, all starting compounds were used without further purification. Tetrakis(triphenylphosphine)palladium(0) [16], triphenyltin hydride [17], *N*,*N*-dimethylaminophenylethyne (**1**) [18], 1-ethoxyhex-1-yne (**3**) [19], ethylthioethyne (**4**) [20], triphenylvinylstannane (**6**) [21] were prepared in accordance with procedures described in the literature.

3.1.3. Synthesis of 1-(methylthio)hept-1-yne (5)

A solution of *n*-BuLi in hexane (1.55 m, 50 ml) was added dropwise to hept-1-yne (7.3 g, 76 mmol) in THF (200 ml) at −78°C. After 10 min dimethyldisulfide (7.2 g, 76 mmol) in THF (15 ml) was added and the reaction mixture was stirred at −78°C for 10 min and for a further 45 min at room temperature. The precipitation of LiSMe was filtered off and CH_2Cl_2 (50 ml)

and sodium chloride solution (10%, 100 ml) was added. The organic layer was separated, washed with KOH (5%, 100 ml) and sodium chloride solutions (10%, 100 ml) and dried over Na_2SO_4. After solvent evaporation under reduced pressure, the residue was distilled at 4 Torr and **5** (4.4 g, yield 41%, purity 99%) was obtained as the fraction boiling at 62–63°C.

^{1}H-NMR: $\delta = 2.33$ (3H, s, SCH_3), 2.26 (2H, t, C≡CCH_2), 1.40–1.59 (2H, m, $CH_2(CH_2)_3CH_3$), 1.21–1.4 (4H, m, $CH_2(CH_2)_3CH_3$), 0.88 (3H, t, $CH_2(CH_2)_3CH_3$). ^{13}C-NMR: $\delta = 93.23$ (C≡CS), 69.74 (C≡CS), 30.96/28.40/22.12/19.12 ($(CH_2)_4CH_3$), 19.96 (SCH_3), 13.88 ($(CH_2)_4CH_3$).

3.2. Syntheses of functionalised vinylstannanes

3.2.1. Non-catalysed hydrostannylation (general procedure)

A mixture of triphenyltin hydride (7.0 g, 20 mmol) and the requisite functionalised acetylene **1**–**5** (22 mmol) in hexane (20 ml) was stirred at 50–55°C for 6–8 h. Then the reaction mixture was worked up as described below.

3.2.2. Pd-catalysed hydrostannylation (general procedure)

Triphenyltin hydride (7.4 g, 21 mmol) in THF (15 ml) was added dropwise to a solution of **1**–**5** (21 mmol) and [Pd(PPh_3)$_4$] (240 mg, 0.21 mmol) in THF (15 ml) at −30°C in the dark. After 30 min, the dark brown reaction mixture was worked up as described below.

3.2.3. Work-up procedures

3.2.3.1. Method a. The solvent was removed in vacuo. The residue was purified by means of preparative HPLC. 5–10 HPLC runs result in about 100 mg of isomerically pure substance starting from 300–500 mg of crude mixture. Fractions were collected in manual mode. When mobile phase was removed in vacuo chloroform (2 × 50 ml) was added and evaporated in vacuo to remove residual mobile phase. The residue was diluted in $CDCl_3$ (0.5 ml) and the solution was transferred to the NMR tube. After characterisation by means of NMR spectroscopy the kinetics measurement was performed (see Section 3.3).

3.2.3.2. Method b. At room temperature the crystals of **4a** were filtered off and recrystallised from hexane (4.5 g, yield 51%, m.p. 86–90°C). The solvent was removed from mother liquor in vacuo. The obtained colourless oil (4.2 g, yield 46%) consisting of **4a** and **4b** (3:4) was further purified by means of preparative HPLC in order to obtain pure **4b** (see above, method a).

3.2.3.3. Method c. The solvent was removed in vacuo. The residue was purified by rapid column chromatography on silicagel, eluting with hexane.

3.2.4. Characterisation of functionalised vinylstannanes

*3.2.4.1. (E)-1-Ethoxy-2-triphenylstannylethene (**2a**)*

Work-up procedure a. Purity 100% (^{1}H-NMR). ^{1}H-NMR: $\delta = 7.25$–7.74 (15H, m, C_6H_5), 6.43 (1H, d, $^3J_{H,H} = 15.6$ Hz, $^3J_{Sn,H} = 42.8$ Hz, SnCH=CH), 4.92 (1H, d, $^3J_{H,H} = 15.6$ Hz, $^2J_{Sn,H} = 52.0$ Hz, SnCH=CH), 3.83 (2H, q, OCH_2CH$_3$), 1.25 (3H, t, OCH$_2$CH_3). ^{13}C-NMR: $\delta = 158.00$ ($^2J_{Sn,C} = 64.8$ Hz, SnCH=C), 138.41 ($^1J_{Sn,C} = 545.0$ Hz, *i*-C), 136.92 ($^2J_{Sn,C} = 37.7$ Hz, *o*-CH), 128.96 ($^4J_{Sn,C} = 13.0$ Hz, *p*-CH), 128.49 ($^3J_{Sn,C} = 52.3$ Hz, *m*-CH), 88.97 ($^1J_{Sn,C} = 540.0$ Hz, SnCH=C), 63.18 (OCH$_2$CH$_3$), 14.53 (OCH$_2$$CH_3$). ^{119}Sn-NMR: $\delta = -116.3$.

*3.2.4.2. (Z)-1-Ethoxy-2-triphenylstannylethene (**2b**)*

Work-up procedure a. Purity 100% (^{1}H-NMR). ^{1}H-NMR: $\delta = 7.25$–7.74 (15H, m, C_6H_5), 6.94 (1H, d, $^3J_{H,H} = 6.8$ Hz, $^3J_{Sn,H} = 127.7$ Hz, SnCH=CH), 4.88 (1H, d, $^3J_{H,H} = 6.8$ Hz, $^2J_{Sn,H} = 62.2$ Hz, SnCH=CH), 3.68 (2H, q, OCH_2CH$_3$), 0.97 (3H, t, OCH$_2$CH_3). ^{13}C-NMR: $\delta = 159.07$ ($^2J_{Sn,C} = 25.5$ Hz, SnCH=C), 139.68 ($^1J_{Sn,C} = 545.0$ Hz, *i*-C), 137.10 ($^2J_{Sn,C} = 38.7$ Hz, *o*-CH), 128.70 ($^4J_{Sn,C} = 11.2$ Hz, *p*-CH), 128.34 ($^3J_{Sn,C} = 52.2$ Hz, *m*-CH), 94.92 ($^1J_{Sn,C} = 510.8$ Hz, SnCH=C), 67.41 (OCH$_2$CH$_3$), 15.18 (OCH$_2$$CH_3$). ^{119}Sn-NMR: $\delta = -135.2$.

*3.2.4.3. 1-Ethoxy-1-triphenylstannylethene (**2c**)*

Work-up procedure a. Purity 98% (^{1}H-NMR). ^{1}H-NMR: $\delta = 7.25$–7.74 (15H, m, C_6H_5), 4.87 (1H, d, $^2J_{H,H} = 1.5$ Hz, $^3J_{Sn,H} = 130.3$ Hz, *trans*-SnC=CH), 4.27 (1H, d, $^2J_{H,H} = 1.5$ Hz, $^3J_{Sn,H} = 41.6$ Hz, *cis*-SnC=CH), 3.90 (2H, q, OCH_2CH$_3$), 1.37 (3H, t, OCH$_2$CH_3). ^{13}C-NMR: $\delta = 169.67$ ($^1J_{Sn,C} = 661.0$ Hz, SnC=CH$_2$), 137.98 ($^1J_{Sn,C} = 540.3$ Hz, *i*-C), 137.10 ($^2J_{Sn,C} = 37.7$ Hz, *o*-CH), 129.11 ($^4J_{Sn,C} = 11.4$ Hz, *p*-CH), 128.49 ($^3J_{Sn,C} = 46.2$ Hz, *m*-CH), 98.67 ($^2J_{Sn,C} = 89.7$ Hz, SnC=CH$_2$), 62.89 (OCH$_2$CH$_3$), 14.48 (OCH$_2$$CH_3$). ^{119}Sn-NMR: $\delta = -161.6$.

*3.2.4.4. (E)-1-Ethoxy-2-triphenylstannylhex-1-ene (**3a**)*

Work-up procedure a. Purity 100% (^{1}H-NMR). ^{1}H-NMR: $\delta = 7.25$–7.74 (15H, m, C_6H_5), 5.93 (1H, s, $^3J_{Sn,H} = 42.0$ Hz, SnC=CH), 3.77 (2H, q, OCH_2CH$_3$), 2.39 (2H, m, $^3J_{Sn,H} = 69.2$ Hz, SnCCH_2CH$_2$), 1.17–1.34 (4H, m, $CH_2(CH_2)_2CH_3$), 1.21 (3H, t, OCH$_2$CH_3), 0.71 (3H, t, CH$_2$CH$_2$CH_3). ^{13}C-NMR: $\delta = 151.95$ ($^2J_{Sn,C} = 100.6$ Hz, SnC=C), 138.99 ($^1J_{Sn,C} = 520.0$ Hz, *i*-C), 137.11 ($^2J_{Sn,C} = 36.8$ Hz, *o*-CH), 128.92 ($^3J_{Sn,C} = 49.4$ Hz, *m*-CH), 128.79 ($^4J_{Sn,C} = 11.0$ Hz, *p*-CH), 112.73 ($^1J_{Sn,C} = 553.5$ Hz, SnC=C), 67.45 (OCH$_2$CH$_3$), 32.68

($^3J_{Sn,C}$ = 12.2 Hz, SnCCH$_2$*C*H$_2$), 28.49 ($^2J_{Sn,C}$ = 26.8 Hz, SnC*C*H$_2$CH$_2$), 22.39 (CH$_2$*C*H$_2$CH$_3$), 15.38 (OCH$_2$*C*H$_3$), 13.70 (CH$_2$CH$_2$*C*H$_3$). ^{119}Sn-NMR: δ = −112.5.

3.2.4.5. (Z)-1-Ethoxy-2-triphenylstannylhex-1-ene ***(3b)***

Work-up procedure a. Purity 93% (^{1}H-NMR). ^{1}H-NMR: δ = 7.25–7.74 (15H, m, C$_6$*H*$_5$), 6.68 (1H, s, $^3J_{Sn,H}$ = 122.7 Hz, SnC=C*H*), 3.61 (2H, q, OC*H*$_2$CH$_3$), 2.17 (2H, m, $^3J_{Sn,H}$ = 67.5 Hz, SnCC*H*$_2$CH$_2$), 1.08–1.32 (4H, m, CH$_2$(C*H*$_2$)$_2$CH$_3$), 0.89 (3H, t, OCH$_2$C*H*$_3$), 0.68 (3H, t, CH$_2$CH$_2$C*H*$_3$). ^{13}C-NMR: δ = 152.15 ($^2J_{Sn,C}$ = 4.5 Hz, SnC=*C*), 139.97 ($^1J_{Sn,C}$ = 523.8 Hz, *i*-*C*), 137.17 ($^2J_{Sn,C}$ = 37.1 Hz, *o*-*C*H), 128.41 ($^4J_{Sn,C}$ = 11.2 Hz, *p*-*C*H), 128.13 ($^3J_{Sn,C}$ = 50.2 Hz, *m*-*C*H), 114.79 ($^1J_{Sn,C}$ = 508.3 Hz, Sn*C*=C), 66.92 (O*C*H$_2$CH$_3$), 33.72 ($^3J_{Sn,C}$ = 13.1 Hz, SnCCH$_2$*C*H$_2$), 31.87 ($^2J_{Sn,C}$ = 31.2 Hz, SnC*C*H$_2$CH$_2$), 22.03 (CH$_2$*C*H$_2$CH$_3$), 14.85 (OCH$_2$*C*H$_3$), 13.65 (CH$_2$CH$_2$*C*H$_3$). ^{119}Sn-NMR: δ = −130.4.

3.2.4.6. (E)-1-Ethoxy-1-triphenylstannylhex-1-ene ***(3c)***

Work-up procedure a. Purity 95% (^{1}H-NMR). ^{1}H-NMR: δ = 7.25–7.74 (15H, m, C$_6$*H*$_5$), 4.90 (1H, t, $^3J_{H,H}$ = 7.0 Hz, $^3J_{Sn,H}$ = 34.5 Hz, SnC=C*H*), 3.72 (2H, q, OC*H*$_2$CH$_3$), 2.25 (2H, m, C=CHC*H*$_2$), 1.22–1.33 (4H, m, CH$_2$(C*H*$_2$)$_2$CH$_3$), 1.08 (3H, t, OCH$_2$C*H*$_3$), 0.87 (3H, t, CH$_2$CH$_2$C*H*$_3$). ^{13}C-NMR: δ = 159.27 ($^1J_{Sn,C}$ = 604.1 Hz, Sn*C*=C), 138.95 ($^1J_{Sn,C}$ = 520.0 Hz, *i*-*C*), 136.97 ($^2J_{Sn,C}$ = 37.4 Hz, *o*-*C*H), 128.97 ($^4J_{Sn,C}$ = 11.4 Hz, *p*-*C*H), 128.58 ($^3J_{Sn,C}$ = 50.7 Hz, *m*-*C*H), 128.77 (SnC=*C*), 68.44 ($^3J_{Sn,C}$ = 26.2 Hz, O*C*H$_2$CH$_3$), 31.86 ($^4J_{Sn,C}$ = 6.2 Hz, SnC=CHCH$_2$*C*H$_2$), 25.32 ($^3J_{Sn,C}$ = 41.2 Hz, SnC=CH*C*H$_2$), 22.41 (CH$_2$*C*H$_2$CH$_3$), 15.37 (OCH$_2$*C*H$_3$), 13.94 (CH$_2$CH$_2$*C*H$_3$). ^{119}Sn-NMR: δ = −149.4.

3.2.4.7. (Z)-1-Ethoxy-1-triphenylstannylhex-1-ene ***(3d)***

Work-up procedure a. Purity 75% (^{1}H-NMR). ^{1}H-NMR: δ = 7.25–7.74 (15H, m, C$_6$*H*$_5$), 5.50 (1H, t, $^3J_{H,H}$ = 7.6 Hz, $^3J_{Sn,H}$ = 126.9 Hz, SnC=C*H*), 3.80 (2H, q, OC*H*$_2$CH$_3$), 1.92 (2H, m, SnC=CHC*H*$_2$), 0.99–1.36 (4H, m, CH$_2$(C*H*$_2$)$_2$CH$_3$), 0.93 (3H, t, OCH$_2$C*H*$_3$), 0.66 (3H, t, CH$_2$CH$_2$C*H*$_3$). ^{119}Sn-NMR: δ = −168.3.

3.2.4.8. (E)-1-Ethylthio-2-triphenylstannylethene ***(4a)***

Work-up procedure b. Purity 100% (^{1}H-NMR). ^{1}H-NMR: δ = 7.25–7.74 (15H, m, C$_6$*H*$_5$), 6.67 (1H, d, $^3J_{H,H}$ = 18.4 Hz, $^3J_{Sn,H}$ = 73.2 Hz, SnCH=C*H*), 6.21 (1H, d, $^3J_{H,H}$ = 18.4 Hz, $^2J_{Sn,H}$ = 75.1 Hz, SnC*H*=CH), 2.75 (2H, q, SC*H*$_2$CH$_3$), 1.27 (3H, t, SCH$_2$C*H*$_3$). ^{13}C-NMR: δ = 143.28 ($^2J_{Sn,C}$ = 24.5 Hz, SnCH=*C*), 138.11 ($^1J_{Sn,C}$ = 539.7 Hz, *i*-*C*), 136.96 ($^2J_{Sn,C}$ = 37.6 Hz, *o*-*C*H), 129.05 ($^4J_{Sn,C}$ = 11.1 Hz, *p*-*C*H), 128.55 ($^3J_{Sn,C}$ = 51.4 Hz, *m*-*C*H), 117.61 ($^1J_{Sn,C}$ = 503.5 Hz, Sn*C*H=C), 24.86 (S*C*H$_2$CH$_3$), 14.01 (SCH$_2$*C*H$_3$). ^{119}Sn-NMR: δ = −130.5. Microanalysis: Found (Calc.): C: 60.88 (60.44); H: 5.08 (5.07); S: 7.25 (7.33).

3.2.4.9. (Z)-1-Ethylthio-2-triphenylstannylethene ***(4b)***

Work-up procedure b and a. Purity 100% (^{1}H-NMR). ^{1}H-NMR: δ = 7.25–7.74 (15H, m, C$_6$*H*$_5$), 7.32 (1H, d, $^3J_{H,H}$ = 11.3 Hz, $^3J_{Sn,H}$ = 167.7 Hz, SnCH=C*H*), 6.38 (1H, d, $^3J_{H,H}$ = 11.3 Hz, $^2J(^{119}Sn,^1H)$ = 73.9 Hz, SnC*H*=CH), 2.61 (2H, q, SC*H*$_2$CH$_3$), 1.16 (3H, t, SCH$_2$C*H*$_3$). ^{13}C-NMR: δ = 146.80 ($^2J_{Sn,C}$ = 9.2 Hz, SnCH=*C*), 138.85 ($^1J_{Sn,C}$ = 542.3 Hz, *i*-*C*), 137.08 ($^2J_{Sn,C}$ = 38.0 Hz, *o*-*C*H), 128.82 ($^4J_{Sn,C}$ = 11.2 Hz, *p*-*C*H), 128.39 ($^3J_{Sn,C}$ = 52.3 Hz, *m*-*C*H), 126.19 ($^1J_{Sn,C}$ = 509.1 Hz, Sn*C*H=C), 28.11 (S*C*H$_2$CH$_3$), 15.40 (SCH$_2$*C*H$_3$). ^{119}Sn-NMR: δ = −149.2.

3.2.4.10. 1-Ethylthio-1-triphenylstannylethene ***(4c)***

Work-up procedure c. Purity 89% (^{1}H-NMR). ^{1}H-NMR: δ = 7.25–7.74 (15H, m, C$_6$*H*$_5$), 5.69 (1H, s, $^3J_{Sn,H}$ = 148.6 Hz, *trans*-SnC=C*H*), 5.40 (1H, s, $^3J_{Sn,H}$ = 71.7 Hz, *cis*-SnC=C*H*), 2.73 (2H, q, SC*H*$_2$CH$_3$), 1.18 (3H, t, SCH$_2$C*H*$_3$). ^{13}C-NMR: δ = 143.79 ($^1J_{Sn,C}$ = 463.5 Hz, Sn*C*=CH$_2$), 137.24 ($^1J_{Sn,C}$ = 542.3 Hz, *i*-*C*), 136.98 ($^2J_{Sn,C}$ = 38.1 Hz, *o*-*C*H), 129.15 ($^4J_{Sn,C}$ = 11.4 Hz, *p*-*C*H), 128.52 ($^3J_{Sn,C}$ = 52.5 Hz, *m*-*C*H), 118.47 ($^2J_{Sn,C}$ = 21.6 Hz, SnC=*C*H$_2$), 25.08 ($^3J_{Sn,C}$ = 25.0 Hz, S*C*H$_2$CH$_3$), 12.81 (SCH$_2$*C*H$_3$). ^{119}Sn-NMR: δ = −135.6.

3.2.4.11. (Z)-1-Methylthio-2-triphenylstannylhept-1-ene ***(5b)***

Work-up procedure c. Purity 92% (^{1}H-NMR). ^{1}H-NMR: δ = 7.25–7.74 (15H, m, C$_6$*H*$_5$), 6.78 (1H, s, $^3J_{Sn,H}$ = 151.3 Hz, SnC=C*H*), 2.31 (2H, m, SnCC*H*$_2$CH$_2$), 2.02 (3H, s, SC*H*$_3$), 1.26 (2H, m, SnCCH$_2$C*H*$_2$), 1.04–1.08 (4H, m, CH$_2$(C*H*$_2$)$_2$CH$_3$), 0.72 (3H, t, CH$_2$CH$_2$C*H*$_3$). ^{13}C-NMR: δ = 148.47 ($^1J_{Sn,C}$ = 505.8 Hz, Sn*C*=C), 139.48 ($^1J_{Sn,C}$ = 523.7 Hz, *i*-*C*), 137.04 ($^2J_{Sn,C}$ = 47.7 Hz, *o*-*C*H), 136.60 (SnC=*C*), 128.67 ($^4J_{Sn,C}$ = 12.9 Hz, *p*-*C*H), 128.29 ($^3J_{Sn,C}$ = 50.5 Hz, *m*-*C*H), 39.98 ($^2J_{Sn,C}$ = 44.4 Hz, SnC*C*H$_2$CH$_2$), 31.10 (*C*H$_2$CH$_2$CH$_3$), 29.88 ($^3J_{Sn,C}$ = 12.5 Hz, SnCCH$_2$*C*H$_2$), 22.15 (CH$_2$*C*H$_2$CH$_3$), 17.50 ($^4J_{Sn,C}$ = 5.6 Hz, S*C*H$_3$), 13.88 (CH$_2$CH$_2$*C*H$_3$). ^{119}Sn-NMR: δ = −143.0.

3.2.4.12. (Z)-1-Methylthio-1-triphenylstannylhept-1-ene ***(5c)***

Work-up procedure c. Purity 97% (^{1}H-NMR). ^{1}H-NMR: δ = 7.25–7.74 (15H, m, C$_6$*H*$_5$), 5.88 (1H, t, $^3J_{H,H}$ = 6.8 Hz, $^3J_{Sn,H}$ = 67.5 Hz, SnC=C*H*), 2.34 (2H, m, C=CHC*H*$_2$), 2.10 (3H, s, SC*H*$_3$), 1.37 (2H, m, C=CHCH$_2$C*H*$_2$), 1.24–1.31 (4H, m, CH$_2$(C*H*$_2$)$_2$CH$_3$), 0.85 (3H, t, CH$_2$CH$_2$C*H*$_3$). ^{13}C-NMR: δ = 146.26 ($^2J_{Sn,C}$ = 34.2 Hz, SnC=*C*), 138.96 ($^1J_{Sn,C}$ = 527.2 Hz, *i*-*C*), 136.91 ($^2J_{Sn,C}$ = 36.8 Hz, *o*-*C*H), 136.04 ($^1J_{Sn,C}$ =

505.6 Hz, Sn*C*=C), 129.09 ($^4J_{Sn,C} = 11.1$ Hz, *p*-*C*H) 128.65 ($^3J_{Sn,C} = 52.7$ Hz, *m*-*C*H), 31.52 ($CH_2CH_2CH_3$), 31.05 ($^3J_{Sn,C} = 52.0$ Hz, SnC=C*H*CH_2), 28.53 (C=CHCH_2CH_2), 22.44 ($CH_2CH_2CH_3$), 18.71 ($^3J_{Sn,C} =$ 24.9 Hz, SCH_3), 14.03 ($CH_2CH_2CH_3$). ^{119}Sn-NMR: $\delta = -135.3$.

3.3. Reactions with acids in $CDCl_3$ and kinetic measurements

Acetic acid or chloroacetic acid (1 M in $CDCl_3$) was added to the organotin substrate (ca. 100 mg) in $CDCl_3$ (ca. 0.5 ml) in an NMR tube. Obtained solutions were ca. 0.2 M in tin substrate and ca. 0.4 M in acid. The courses of reaction were followed by means of ^{1}H- and ^{119}Sn-NMR spectroscopy. Gas samples from the NMR tube were analysed by means of gas chromatography for **2a**, **2b**, **4a** and **4b**.

For kinetic mesurements (**2a**, **2b**, **3a**, **3b**, **4a**, and **4b**) the exact amount of HMDS (5 μl) was also added and ^{1}H-NMR spectra were measured in particular intervals. Integral intensities of selected signals and consequently exact concentrations of reagents were referred to internal HMDS standard. Then plots of $\ln(b - x_t)/(a - x_t)$, where a is the starting concentration of the tin substrate, b is the starting concentration of acetic acid and x_t is conversion at a particular time, versus time were obtained and second-order rate constants were calculated from the slope of this correlation in the usual way.

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