REINVESTIGATION OF REACTION OF (2-ETHOXYVINYL)STANNANES WITH ACETYL BROMIDE

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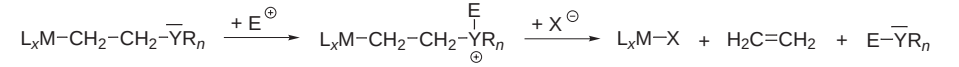
Four analogous (2-ethoxyvinyl)stannanes (*E*/*Z*)-$Bu_3SnC(R)=CHOEt$ (R = Bu, H) were prepared and characterised using ^1H, ^{13}C, ^{119}Sn, ^1H-^{13}C HMQC, ^1H-^{13}C HMBC, and ^1H-^{119}Sn HMQC NMR spectroscopy. The course of their reactions with acetyl bromide was studied by NMR spectroscopy. Although tributyltin bromide, ethyl acetate and the coresponding alkyne were identified as reaction products, this present reinvestigation showed unambiguously that heterolytic fragementation reactions, as stated previously, did not take place. Acetyl bromide cleaves the Sn–C= bond yielding tributyltin bromide and vinyl ethers. Subsequent decomposition of vinyl ethers and impurities in the starting stannane is the source of ethyl acetate and the alkyne, respectively.

Keywords: Tin; Stannanes; Reaction mechanisms; Kinetics; NMR spectroscopy; Tin–carbon bond cleavage; Heterolytic fragmentation.

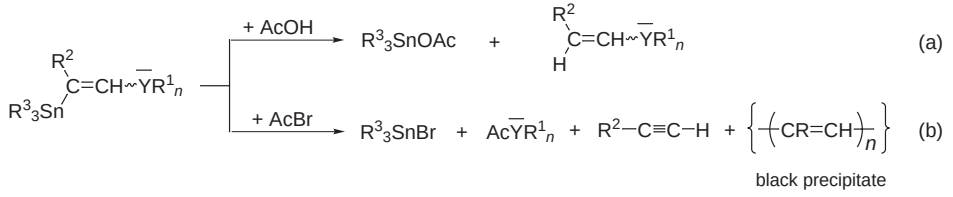
If organometallic compounds with 2-substituted ethyl ligands, where the substituent is a Lewis base, $L_xM–CH_2–CH_2–YR_n$ (YR_n = NR_2, OR, Cl, ...; R = alkyl, aryl, H) are treated with suitable electrophiles, they may undergo elimination reactions, called heterolytic fragmentations[1] (Scheme 1).



SCHEME 1

On the other hand, in organotin compounds with 2-substituted vinyl ligands $Ph_3SnC(R^2)=CHYR^1_n$ (YR^1_n = NMe_2, OEt, SMe, SEt; R^2 = Ph, Bu, pentyl, H), the electrophile (acetic acid) attacks preferably α-carbon atom and a cleavage of the Sn–C= bond takes place[2] (Scheme 2a). In 1975 Kazankova *et al.*[3] classified reactions of (2-substituted vinyl)stannanes $R^3_3SnC(R^2)=CHYR^1_n$ (R^1, R^2, R^3 = alkyl, H; Y = O, N; *n* = 1, 2) with acetyl bromide on the basis of

qualitative analysis of reaction products as heterolytic fragmentation (Scheme 2b).



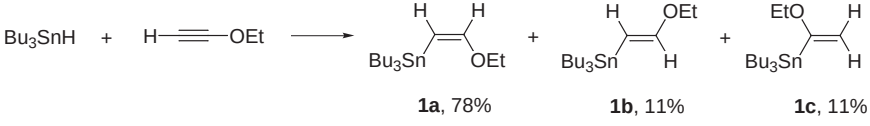
SCHEME 2

These inconsistent findings prompted us to reinvestigate the work of Kazankova. Thus, four (2-substituted vinyl)stannanes (*E/Z*)-$Bu_3SnC(R)$=CHOEt (R = Bu, H) was prepared and characterised using ^1H, ^{13}C, ^{119}Sn, ^1H-^{13}C HMQC (ref.[4]), ^1H-^{13}C HMBC (ref.[5]) and ^1H-^{119}Sn HMQC (ref.[6]) NMR spectroscopy. The course of their reactions with acetyl bromide was studied by NMR spectroscopy.

RESULTS AND DISCUSSION

Synthesis and Characterisation of (2-Ethoxyvinyl)stannanes

In accordance with Kazankova *et al.*[3a], radical hydrostannylation of ethoxyethyne with tributyltin hydride yielded (*Z*)-Bu_3SnCH=CHOEt (**1a**) with rather high regio- and stereoselectivity (Scheme 3).

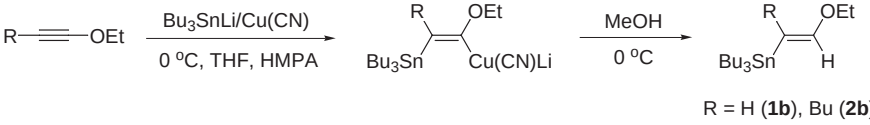


SCHEME 3

On the other hand, radical hydrostannylation of 1-ethoxyhex-1-yne with tributyltin hydride showed very low selectivity. Vacuum distillation of the crude reaction mixture afforded a colourless liquid (**2**). ^{119}Sn NMR spectrum showed that the mixture consists of (*Z*)-$Bu_3SnC(Bu)$=CHOEt (**2a**; 10%), (*E*)-$Bu_3SnC(Bu)$=CHOEt (**2b**; 8%), (*Z*)-$Bu_3SnC(OEt)$=CHBu (**2c**; 12%), (*E*)-$Bu_3SnC(OEt)$=CHBu (**2d**; 43%), $Bu_3SnC{\equiv}CBu$ (**3**; 18%), Bu_6Sn_2 (6%), Bu_3SnOEt (3%).

Moreover, *E*-isomers (*E*)-Bu_3SnCH=CHOEt (**1b**) and (*E*)-$Bu_3SnC(Bu)$=CHOEt (**2b**) were synthesised regio- and stereoselectively by stannylcupration of

ethoxyethyne and 1-ethoxyhex-1-yne with tributyltin hydride in 45 and 50% yields, respectively[7] (Scheme 4).



SCHEME 4

(2-Ethoxyvinyl)stannanes obtained in pure state (**1a**, **1b** and **2b**) were fully characterised by conventional ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. In the complex mixture of products **2**, ^{1}H NMR spectrum proved the presence of all four possible isomers[2] **2a**–**2d** (Fig. 1). For vinyl groups, the assignment of ^{1}H and ^{13}C resonances was achieved by 2D ^{1}H-^{13}C HMQC (Fig. 2a) and HMBC (Fig. 2b). These techniques also allowed to derive corresponding $^{2}J(^{119}Sn,^{13}C)$ and $^{1}J(^{119}Sn,^{13}C)$ coupling constants.

However, ^{119}Sn NMR spectrum indicated that the mixture **2** consisted of seven organotin compounds ($\delta(^{119}Sn)$ 103.0, –32.1, –45.4, –55.8, –61.2, –68.4, –82.8 ppm). The tin resonances at –32.1, –45.4, –55.9 and –61.2 ppm were unambiguously assigned using the ^{1}H-^{119}Sn HMQC spectrum to **2b**, **2a**, **2d** and **2c**, respectively (Fig. 2c). Most likely, ^{119}Sn chemical shifts at –82.6 ppm correspond to Bu_6Sn_2 (ref.[8]). The tin resonance at 103.0 ppm could correspond to Bu_3SnOEt (ref.[9]). However, this type of compound has strongly concentration dependent ^{119}Sn chemical shift. Thus, the assignment is not ambiguous. The ^{119}Sn resonance at –68.4 ppm, which is characteristic of stannylalkynes[10], reveals clear correlation with proton resonance at 2.24 ppm. Thus, these signals were assigned to 1-(tributylstannyl)hex-1-yne (**3**) which was additionally synthesised as a reference substance in order to make the identification indisputable.

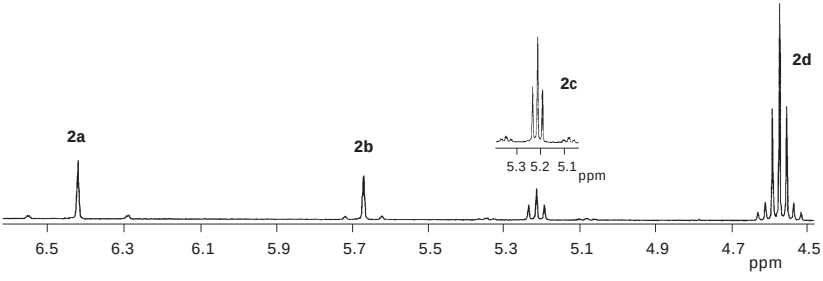


FIG. 1

Partial ^{1}H NMR spectrum of mixture of products **2** obtained by radical hydrostannylation of 1-ethoxyhex-1-yne with tributyltin hydride

Study of Reactivity

The reactions of vinylstannanes (**1a**, **1b**, **2a**) with acetyl bromide afforded tributyltin bromide, ethyl acetate and a black precipitate. If the complex mixture **2** was treated with acetyl bromide in the same way, hex-1-yne was also formed as a minor product (about 5%) in addition to major products mentioned above. So far, the observations have been in agreement with the results of Kazankova *et al.*[3]

For **1a**, the course of reaction was monitored by ^{1}H NMR spectroscopy (Fig. 3). In the beginning, the decays of **1a** and acetyl bromide were consistent with second-order kinetics (Fig. 4). Moreover, ^{119}Sn NMR spectroscopic investigations showed that decay of **1a** is approximately equal to increments of tributyltin bromide. On the contrary, the concentration of ethyl acetate suddenly increased only when **1a** disappeared from the reaction mixture. The sudden increment of ethyl acetate goes parallel with a sudden decrease in acetyl bromide concentration. An analogous course of the reaction was also observed for **1b** and **2b**. These results shoved that ethyl acetate cannot be a product of heterolytic fragmentation. It is probably formed in a subsequent reaction involving acetyl bromide.

Taking into consideration that mixture **2** contains 1-(tributylstannyl)-hex-1-yne (**3**; 18%), the hex-1-yne formation in the reaction of **2** with acetyl bromide does not prove either that heterolytic fragmentation takes

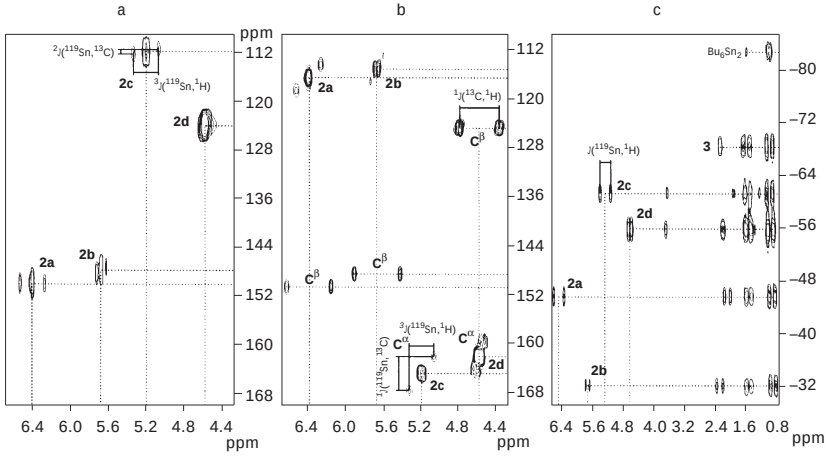


FIG. 2
2D ^{1}H-^{13}C HMQC (a), ^{1}H-^{13}C HMBC (b) and ^{1}H-^{119}Sn HMQC (c) spectra of mixture of products **2** obtained by radical hydrostannylation of 1-ethoxyhex-1-yne with tributyltin hydride

place. Hydrogen bromide and acetic acid, which can form in the reaction mixture due to partial hydrolysis of acetyl bromide, can easily cleave the Sn–C bond in **3** affording hex-1-yne (Scheme 5). Since the reaction of acetyl bromide with pure **2b** did not afford any hex-1-yne, it is highly probable that the source of hex-1-yne is not heterolytic fragmentation but the reaction mentioned above.

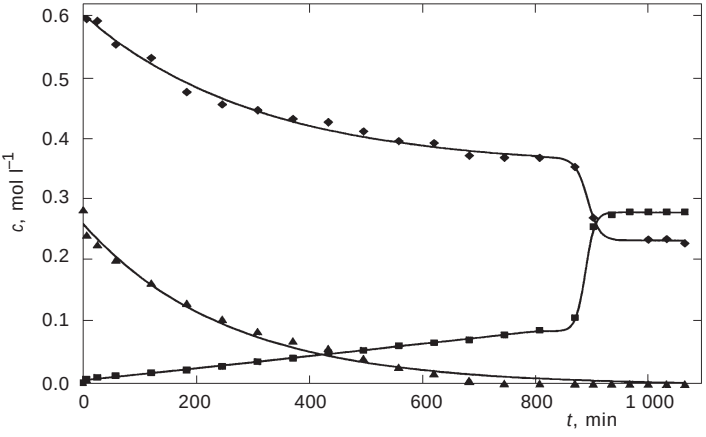


FIG. 3
Dependence of concentrations of (*Z*)-$Bu_3SnCH{=}CHOEt$ (**1a**; ▲), acetyl bromide (◆) and ethyl acetate (■) on time monitored by means ^1H NMR

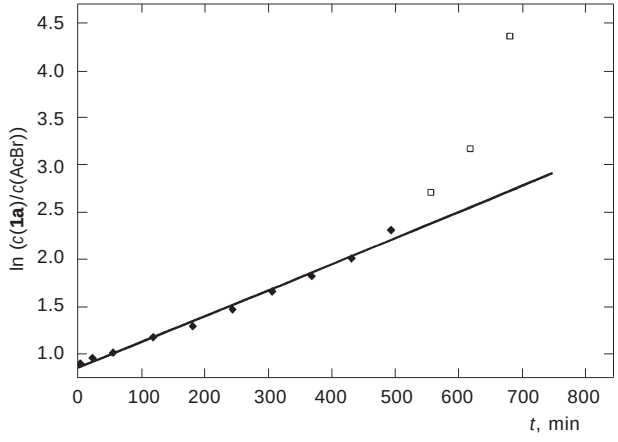
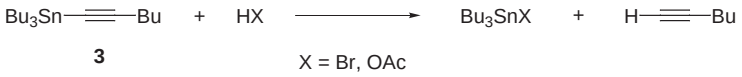
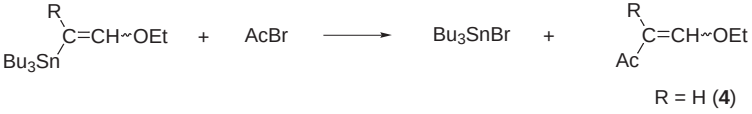


FIG. 4
Verification of second-order kinetics for reaction of (*Z*)-$Bu_3SnCH{=}CHOEt$ (**1a**) with acetyl bromide. Data consistent (◆) and inconsistent (❑) with second-order kinetics



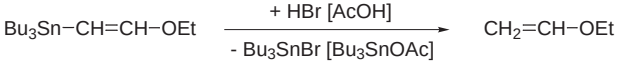
SCHEME 5

Considering that in (2-substituted vinyl)stannanes $Ph_3SnC(R^2)=CHYR^1_n$ (Y = O, S or N), α-carbon of the vinyl group is more susceptible to electrophilic attack than the basic heteroatom Y, it can be proposed that acetyl bromide as electrophile reacts with (2-ethoxyvinyl)stannanes analogously[2] (Scheme 6). Therefore, the prospective product of reaction of **1b** with acetyl bromide, (*E*)-4-ethoxybut-3-ene-2-one (**4**), was synthesised as reference substance.



SCHEME 6

Monitoring of reactions of (2-ethoxyvinyl)stannanes (**1a**, **1b**) with acetyl bromide by ^{1}H NMR spectroscopy indicated that ethyl vinyl ether is formed by partial hydrolysis of acetyl bromide and subsequent cleavage of the Sn–C bond with hydrogen bromide or else with acetic acid (Scheme 7). However, attempts to prove the presence of **4** in the reaction mixture by ^{1}H and ^{13}C NMR spectroscopy failed. The concentration of **4** may be very low during the reaction because its formation is probably significantly slower than decomposition. It was found that **4** treated with acetyl bromide readily undergoes decomposition affording a black precipitate and a almost stoichiometric amount of ethyl acetate. The course of this reaction seems to be rather complex – it probably involves polymerisation – and remains unclear. An analogous reaction was also observed for ethyl vinyl ether.



SCHEME 7

In the reaction of **1a** with acetyl bromide, a black precipitate was isolated. Elemental analysis (56.15% C, 5.89% H, 24.05% Br) unambiguously proved that it was not polyacetylene as stated by Kazankova *et al.*[3] Elemental analyses of the black precipitates afforded by reactions of acetyl bromide with ethyl vinyl ether (49.41% C, 4.76% H, 36.43% Br) and **4** (37.06% C, 4.86% H, 48.14% Br) do not correspond to that of the precipitate rising from **1a**.

However, significant contents of bromine were found in all cases. Regarding their formation, the black precipitates could hardly be considered chemically individual substances. Thus, further attempts to identify this stuff would be pointless. Nevertheless, the decomposition of vinyl ethers mentioned above seems to be subsequent reaction which affords ethyl acetate and the black precipitate when (2-ethoxyvinyl)stannanes are treated with acetyl bromide.

CONCLUSIONS

This paper unambiguously proves that the reactions of (2-ethoxyvinyl)-stananes with acetyl bromide cannot be considered heterolytic fragmentation though the reactions afford tributyltin bromide, ethyl acetate and an alkyne, *i.e.* prospective products of heterolytic fragmentation (Scheme 2b). Acetyl bromide, as well as hydrogen bromide, formed by hydrolysis of acetyl bromide in the reaction mixture, cleaves the Sn–C= bond yielding tributyltin bromide and vinyl ethers. Likely, decomposition of those vinyl ethers is the source of ethyl acetate and of the black precipitate which was incorrectly identified[3] as polyacetylene. Thus, only qualitative analysis of products, even though the requisite alkyne was formed, cannot be considered as a proof of a heterolytic fragmentation reaction. The present work shows that in the case described in literature[3], impurities in the starting material most probably gave rise to erroneous conclusions.

EXPERIMENTAL

Methods

Elemental analyses (C, H, Br) were carried out using a Fison EA 1108 instrument in the Microanalytical Laboratory of the University. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded using a 5 mm tunable probehead on a Bruker AMX 360 (^{1}H 360.14 MHz, ^{13}C 90.57 MHz, ^{119}Sn 134.28 MHz) in $CDCl_3$ at 300 K. ^{1}H-^{13}C gs HMQC (ref.[4]), ^{1}H-^{13}C gs HMBC (ref.[5]) and ^{1}H-^{119}Sn gs HMQC (ref.[6]) were recorded on a Bruker AMX 360 spectrometer using a 5 mm inverse probehead with Z-gradient shielding. ^{1}H, ^{13}C and ^{119}Sn chemical shifts are given in ppm relative to Me_4Si and Me_4Sn, respectively, coupling constants (J) in Hz.

(2-Ethoxyvinyl)stannanes

(2-Ethoxyvinyl)stannanes were prepared by radical hydrostannylation (**1a**, **2**) and stannylcupration (**1b**, **2b**) described in ref.[3a] and ref.[7], respectively.

Tributyl((Z)-2-ethoxyvinyl)stannane (**1a**). ^{1}H NMR: 6.75 d, 1 H, $^{3}J_{HH}$ = 7.2, $^{3}J_{SnH}$ = 105.5 (SnCH=C**H**); 4.48 d, 1 H, $^{3}J_{HH}$ = 7.2, $^{2}J_{SnH}$ = 54.0 (SnC**H**=CH); 3.75 q, 2 H, $^{3}J_{HH}$ = 7.1 (OC$\mathbf{H}_2$CH$_3$); 0.65–1.52 m, 30 H ((C$\mathbf{H}_3$(C$\mathbf{H}_2$)$_3$)$_3$Sn, OCH$_2$C$\mathbf{H}_3$). ^{13}C NMR: 157.0, $^{2}J_{SnC}$ = 21.3

(SnCH=C**H**); 97.7, $^{1}J_{SnC}$ = 367.7 (Sn**C**H=CH); 66.7 (O**C**H_2CH_3); 29.2, $^{2}J_{SnC}$ = 20.6 (SnCH_2**C**H_2CH_2); 27.3, $^{3}J_{SnC}$ = 56.9 (Sn(CH_2)$_2$**C**H_2CH_3); 15.2 (OCH_2**C**H_3); 13.7 (Sn(CH_2)$_3$**C**H_3); 10.1, $^{1}J_{SnC}$ = 350.9 (SnCH_2). ^{119}Sn NMR: –48.0.

Tributyl((E)-2-ethoxyvinyl)stannane (**1b**). ^{1}H NMR: 6.20 d, 1 H, $^{3}J_{HH}$ = 15.6, $^{3}J_{SnH}$ = 35.6 (SnCH=C**H**); 4.61 d, 1 H, $^{3}J_{HH}$ = 15.6, $^{2}J_{SnH}$ = 41.0 (SnC**H**=CH); 3.78 q, 2 H, $^{3}J_{HH}$ = 7.5 (OC$\mathbf{H}_2$CH_3); 0.65–1.52 m, 30 H ((C$\mathbf{H}_3$(C$\mathbf{H}_2$)$_3$)$_3$Sn, OCH_2C$\mathbf{H}_3$). ^{13}C NMR: 154.6, $^{2}J_{SnC}$ = 49.3 (SnCH=**C**H); 91.5, $^{1}J_{SnC}$ = 391.1 (Sn**C**H=CH); 62.6 (O**C**H_2CH$_3$); 29.0, $^{2}J_{SnC}$ = 20.6 (SnCH_2**C**H_2CH_2); 27.2 $^{3}J_{SnC}$ = 54.8 (Sn(CH_2)$_2$**C**H_2CH_3); 14.5 (OCH_2**C**H_3); 13.6 (Sn(CH_2)$_3$**C**H_3); 9.6, $^{1}J_{SnC}$ = 350.8 (Sn**C**H_2). ^{119}Sn NMR: –33.4.

Tributyl(1-ethoxyvinyl)stannane (**1c**). ^{1}H NMR: 4.66 d, 1 H, $^{2}J_{HH}$ = 2, $^{3}J_{SnH}$ = 100.0 (*trans*-SnC=CH); 4.03 d, 1 H, $^{2}J_{HH}$ = 2, $^{3}J_{SnH}$ = 41.0 (*cis*-SnC=CH); 3.68 q, 2 H, $^{3}J_{HH}$ = 7.0 (OC$\mathbf{H}_2$CH_3); 0.65–1.52 m, 30 H ((C$\mathbf{H}_3$(C$\mathbf{H}_2$)$_3$)$_3$Sn, OCH_2C$\mathbf{H}_3$). ^{13}C NMR: 172.9, $^{1}J_{SnC}$ = 483.4 (Sn**C**=CH_2); 95.4, $^{2}J_{SnC}$ = 71.8 (SnC=**C**H_2); 62.0 (O**C**H_2CH$_3$); 29.0, $^{2}J_{SnC}$ = 20.9 (SnCH_2**C**H_2CH_2); 27.2, $^{3}J_{SnC}$ = 54.9 (Sn(CH_2)$_2$**C**H_2CH_3); 14.6 (OCH_2**C**H_3); 13.7 (Sn(CH_2)$_3$**C**H_3); 9.3, $^{1}J_{SnC}$ = 343.1 (Sn**C**H_2). ^{119}Sn NMR: –58.7.

Tributyl((Z)-1-ethoxyhex-1-en-2-yl)stannane (**2a**). ^{1}H NMR: 6.42 s, 1 H, $^{3}J_{SnH}$ = 95.8 (SnC=CH); 3.67 q, 2 H, $^{3}J_{HH}$ = 7.1 (OC$\mathbf{H}_2$CH_3); 2.05 m, 2 H, $^{3}J_{SnH}$ = 55.2 (SnCC$\mathbf{H}_2$CH_2); 0.65–1.52 m, 37 H ((C$\mathbf{H}_3$(C$\mathbf{H}_2$)$_3$)$_3$SnCCH$_2$(C$\mathbf{H}_2$)$_2$C$\mathbf{H}_3$, OCH_2C$\mathbf{H}_3$). ^{13}C NMR: 150.7 (SnC=**C**H); 116.6, $^{1}J_{SnH}$ = 390 (Sn**C**=CH); 66.5 (O**C**H_2CH$_3$); 32.8 (SnC**C**H_2CH_2). ^{119}Sn NMR: –45.4.

Tributyl((E)-1-ethoxyhex-1-en-2-yl)stannane (**2b**). ^{1}H NMR: 5.67 s, 1 H, $^{3}J_{SnH}$ = 35.8 (SnC=CH); 3.76 q, 2 H, $^{3}J_{HH}$ = 7.0, (OC$\mathbf{H}_2$CH_3); 2.24 m, 2 H, $^{3}J_{SnH}$ = 56.3 (SnCC$\mathbf{H}_2$CH_2); 0.65–1.52 m, 37 H ((C$\mathbf{H}_3$(C$\mathbf{H}_2$)$_3$)$_3$SnCCH$_2$(C$\mathbf{H}_2$)$_2$C$\mathbf{H}_3$, OCH_2C$\mathbf{H}_3$). ^{13}C NMR: 148.5, $^{2}J_{SnC}$ = 78.1 (SnC=**C**H); 114.8, $^{3}J_{SnC}$ = 407.5 (Sn**C**=CH); 66.7 (O**C**H_2CH$_3$); 32.8, $^{3}J_{SnC}$ = 9.9 (SnCCH_2**C**H_2); 29.1, $^{2}J_{SnC}$ = 19.4 (SnCH_2**C**H_2CH_2); 28.6, $^{2}J_{SnC}$ = 21.8 (SnC**C**H_2CH_2); 27.3, $^{3}J_{SnC}$ = 56.2 (Sn(CH_2)$_2$**C**H_2CH_3); 22.5 (SnC(CH_2)$_2$**C**H_2CH_3); 15.2 (OCH_2**C**H_3); 13.9 (SnC(CH_2)$_3$**C**H_3); 13.6 (Sn(CH_2)$_3$CH_3); 9.5, $^{1}J_{SnC}$ = 336.7 (Sn**C**H_2). ^{119}Sn NMR: –32.1.

Tributyl((Z)-1-ethoxyhex-1-en-1-yl)stannane (**2c**). ^{1}H NMR: 5.21 t, 1 H, $^{3}J_{SnH}$ = 97.0, $^{3}J_{HH}$ = 7.5 (SnC=CH); 3.62 q, 2 H, $^{3}J_{HH}$ = 7.1 (OC$\mathbf{H}_2$CH_3); 1.88 m, 2 H (C=CHCC$\mathbf{H}_2$CH_2); 0.65–1.52 m, 37 H ((C$\mathbf{H}_3$(C$\mathbf{H}_2$)$_3$)$_3$SnCCH$_2$(C$\mathbf{H}_2$)$_2$C$\mathbf{H}_3$, OCH_2C$\mathbf{H}_3$). ^{13}C NMR: 164.9, $^{1}J_{SnH}$ = 504 (Sn**C**=CH); 111.9, $^{2}J_{SnC}$ = 72 (SnC=**C**H); 34.1 (SnCCH$_2$**C**H_2CH_2); 29.7 (SnC**C**H_2CH_2). ^{119}Sn NMR: –61.2.

Tributyl((E)-1-ethoxyhex-1-en-1-yl)stannane (**2d**). ^{1}H NMR: 4.58 t, 1 H, $^{3}J_{HH}$ = 6.8, $^{3}J_{SnH}$ = 27.3 (SnC=CH); 3.65 q, 2 H, $^{3}J_{HH}$ = 7.0 (OC$\mathbf{H}_2$CH_3); 2.16 m, 2 H (C=CHC$\mathbf{H}_2$CH_2); 0.65–1.52 m, 37 H ((C$\mathbf{H}_3$(C$\mathbf{H}_2$)$_3$)$_3$Sn, C=CHCH$_2$(C$\mathbf{H}_2$)$_2$C$\mathbf{H}_3$, OCH_2C$\mathbf{H}_3$). ^{13}C NMR: 162.1, $^{1}J_{SnC}$ = 435.6 (Sn**C**=CH); 124.7, $^{2}J_{SnC}$ = 80.4 (SnC=**C**H); 67.3, $^{4}J_{SnC}$ = 21.9 (O**C**H_2CH$_3$); 32.1 (SnCCH$_2$**C**H_2); 29.0, $^{2}J_{SnC}$ = 19.9 (SnCH_2**C**H_2CH_2); 27.3, $^{3}J_{SnC}$ = 58.5 (Sn(CH_2)$_2$**C**H_2CH_3); 24.9, $^{4}J_{SnC}$ = 32.2 (C=CH**C**H_2CH_2); 22.4 (CHC(CH_2)$_2$**C**H_2CH_3); 15.6 (OCH_2**C**H_3); 13.9 (CH(CH_2)$_3$**C**H_3); 13.6 (Sn(CH_2)$_3$**C**H_3); 10.8, $^{1}J_{SnC}$ = 334.3 (Sn**C**H_2). ^{119}Sn NMR: –55.8.

Tributyl(hex-1-yn-1-yl)stannane (**3**)

Butyllithium in hexane (1.56 M; 17.9 ml, 30 mmol) was added to a solution of hex-1-yne (2.3 g, 30 mmol) in THF (50 ml) at –78 °C. After 20 min the reaction mixture was warmed up to room temperature and water (50 ml) and Et_2O (100 ml) were added. The organic layer was separated and dried over anhydrous Na_2SO_4. Evaporation of solvents *in vacuo* afforded a colourless oil which was further purified by vacuum distillation (b.p. 87–88 °C/5 Pa). The product (7.6 g, 68%) was of purity higher than 95%. ^{1}H NMR: 2.22 t, 2 H (≡CCH_2); 1.28–1.59 m, 16 H (CH_2(C$\mathbf{H}_2$)$_2$CH_3); 0.92 m, 6 H (SnCH_2); 0.91 t, 3 H (≡C(CH_2)$_3$C$\mathbf{H}_3$); 0.89 t,

9 H ($Sn(CH_2)_3CH_3$). ^{13}C NMR: 111.6, $^2J_{SnC}$ = 72.5 ($SnC{\equiv}C$); 80.9, $^1J_{SnC}$ = 382.2 ($SnC{\equiv}C$); 31.2 ($\equiv CCH_2CH_2$); 28.8, $^2J_{SnC}$ = 22.8 ($SnCH_2CH_2$); 26.9, $^3J_{SnC}$ = 58.4 ($SnCH_2CH_2CH_2$); 21.7 ($\equiv CCH_2CH_2CH_2$); 19.7, $^3J_{SnC}$ = 8.4 ($\equiv CCH_2$); 13.5 ($Sn(CH_2)_3CH_3$); 13.4 ($\equiv C(CH_2)_3CH_3$); 10.8, $^1J_{SnC}$ = 384.0 ($SnCH_2$). ^{119}Sn NMR: –68.4.

(*E*)-4-Ethoxybut-3-ene-2-one (**4**)

Compound **4** was prepared from acetone, ethyl formate and ethyl bromide according to ref.[11]. ^1H NMR: 7.44 d, 1 H, $^3J_{HH}$ = 12.8 ($CH{=}CHOCH_2$); 5.48 d, 1 H, $^3J_{HH}$ = 12.8 ($COCH{=}CH$); 3.84 q, 2 H, $^3J_{HH}$ = 7.1 (OCH_2CH_3); 2.07 s, 3 H (CH_3CO); 1.24 t, 3 H, $^3J_{HH}$ = 7.1. ^{13}C NMR: 197.0 (CH_3CO); 162.2 ($CH{=}CHOCH_2$); 106.9 ($COCH{=}CH$); 66.7 (OCH_2CH_3); 27.4 (CH_3CO); 14.1 (OCH_2CH_3).

Reactions with Acetyl Bromide in $CDCl_3$ and Kinetic Measurements

$CHCl_3$ (10 μl) and about 2 equivalents of acetyl bromide were added to the substrate (*ca* 0.1 g for **1a**, **1b**, **2b** and *ca* 0.05 g for **4**) in $CDCl_3$ (*ca* 0.5 ml) in an NMR tube under argon atmosphere. ^1H and ^{119}Sn NMR spectra were measured at regular intervals. Integral intensities of selected signals were referred to internal $CHCl_3$ standard.

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REFERENCES

1. a) Grob C. A., Schiess P. W.: *Angew. Chem.* **1967**, *79*, 1; b) Grob C. A.: *Angew. Chem.* **1969**, *81*, 543; c) Weichmann H., Tzschach A.: *Z. Anorg. Allg. Chem.* **1979**, *458*, 291; d) Steinborn D., Sedlak U., Taube R.: *Z. Anorg. Allg. Chem.* **1982**, *492*, 103; e) Davis D. D., Gray C. E.: *J. Org. Chem.* **1970**, *35*, 1303.
2. Lébl T., Holeček J., Dymák M., Steinborn D.: *J. Organomet. Chem.* **2001**, *625*, 86; and references therein.
3. a) Kazankova M. A., Zverkova T. I., Levin M. Z., Lutsenko I. F.: *Zh. Obshch. Khim.* **1975**, *45*, 73; b) Kazankova M. A., Zverkova T. I., Lutsenko I. F.: *Zh. Obshch. Khim.* **1975**, *45*, 2044.
4. Bax A., Griffey R. H., Hawkins B. H.: *J. Magn. Reson.* **1983**, *55*, 301.
5. Bax A., Summers M. F.: *J. Am. Chem. Soc.* **1986**, *108*, 2093.
6. Martins J. C., Biesemans M., Willem R.: *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 271.
7. Cabezas J. A., Oehlschlager A. C.: *Synthesis* **1994**, 432.
8. Lehnig M., Neumann W. P., Seifert P.: *J. Organomet. Chem.* **1978**, *162*, 145.
9. Smith P. J., White R. F. M., Smith L.: *J. Organomet. Chem.* **1972**, *40*, 341.
10. a) Wrackmeyer B.: *J. Magn. Reson.* **1981**, *42*, 287; b) Mitchell T. N.: *J. Organomet. Chem.* **1977**, *141*, 289; c) Wrackmayer B.: *J. Organomet. Chem.* **1979**, *166*, 353.
11. Spassky-Pasteur A., Riviére H.: *Bull. Soc. Chim. Fr.* **1969**, 811.