Kinetics of Protodestannylation of Substituted Vinylstannanes

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ABSTRACT

The set of vinylstannanes of general formula (*E*)/(*Z*)-$R_3SnC(R')=CHR''$ ($R_3Sn/R'/R''$ = Ph_3Sn/H/OEt **1a/1b**, Bu_3Sn/H/OEt **2a/2b**, Bu_2ClSn/H/OEt **3a/3b**, Bu_3Sn/OEt/OEt **4a**, Bu_3Sn/H/Bu **5a/5b**, Bu_3Sn/H/*t*-Bu **6a/6b**, Bu_3Sn/H/Ph **7a/7b**, Bu_3Sn/H/H **8**) was prepared and the kinetics of reactions with acetic, chloroacetic and trifluoroacetic acid in $CDCl_3$ at 25°C were studied by means of ^1H NMR spectroscopy in order to find an explanation of the difference in reactivity of stereoisomers. The reaction starts with the rate determining step whereat the proton of carboxylic acid attacks the α-carbon of the double bond and consequently the transition state rises, where a positive charge is developed partly at the tin atom and partly at the β-carbon of the double bond. It was shown that the stabilisation of this positive charge is at least as significant for the overall rate of reaction as an electron density on the α-carbon of vinyl group. Furthermore, it was suggested that for weak acids the nucleophilic assistance of the anionic moiety to the departing tin atom takes place and that this is probably responsible for the difference in reactivity of *E*- and *Z*-isomers. It is supposed that, due to conjugation of the tin atom with the π-electron system of the vinyl group, mutual *trans*-position of an electron-releasing substituent (OEt or alkyl) and the tin centre makes this nuclecleophilic assistance easier than in the case of mutual *cis*-position, while an electron-withdrawing substituent (Ph) has the reverse effect.

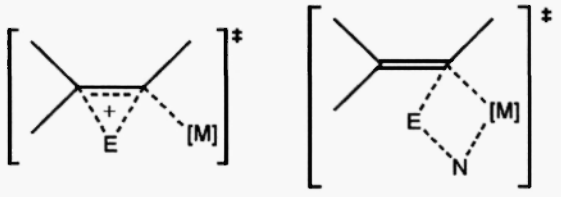
Keywords: Functionalised vinylstannanes; Protodestannylation; NMR; Kinetics; Nucleophilic assistance

1. INTRODUCTION

Protodestannylation can be classified as electrophilic substitution involving cleavage of a carbon-tin bond by a proton. So far, electrophilic demetallation was studied in a number of organometallic compounds of group 4 or mercury, whereas not only various acids but also other electrophilic agents (bromine, iodine, mercuric halides etc.) have been used /1/. The rate-determining step of this reaction is predominantly the attack of electrophile at the carbon bonded to metal and thus the reaction can be described mechanistically as S_E2. If a vinyl or aryl group is cleaved, the electrophilic attack takes place at the unsaturated carbon and the

cleavage is much easier than for an alkyl group where an electrophile attacks saturated carbon. The exception holds for allylic substrates, where the mechanism starts with the attack of electrophile at the unsaturated γ-carbon and thus can be denoted as S_E2'. The cleavage of allyl group is therefore even easier than in the case of vinyl or aryl group.

Since electrophilic demetallation of vinylmetallic compounds proceeds with retention of configuration, closed three-center (Scheme 1A) /2/ and four-center (Scheme 1B) /3/ transition states were supposed in early studies.

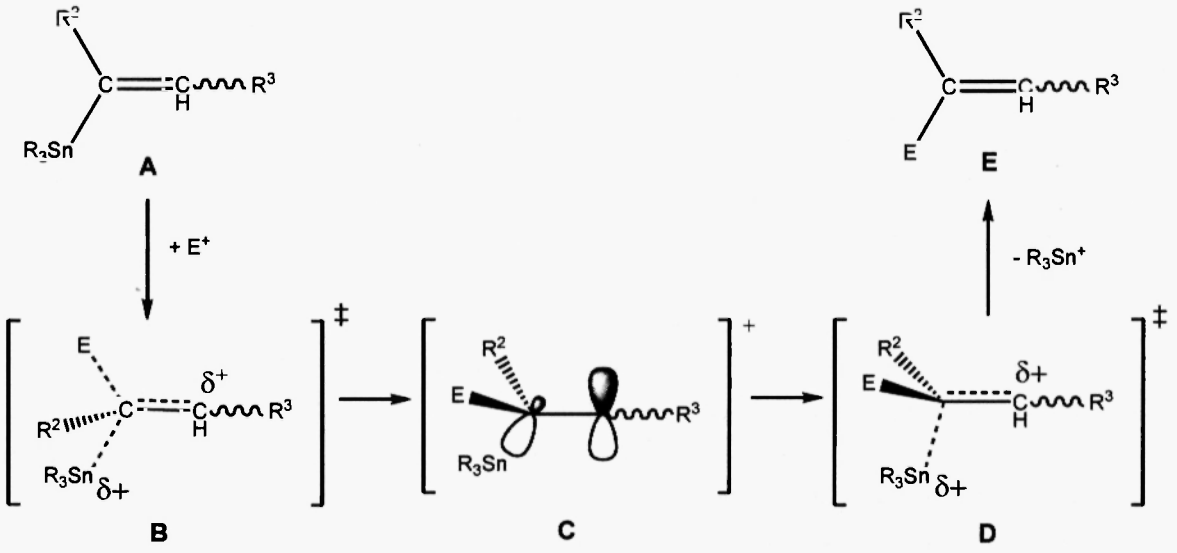


A B

Scheme 1 Closed three- and four-centre transition states supposed in early studies of electrophilic demetallation of vinylmetallic compounds

However, the later reports of Abraham /4/, Baekelmans /5/, Eaborn /6/ and Cochran /7/ exclude the formation of closed transition states and make it possible to suggest the mechanism which is depicted in Scheme 2.

The reaction starts with the rate-determining step where an electrophile attacks the α-carbon of the double bond, and consequently the transition state **B** arises where a positive charge is developed partly at the tin atom and partly at the β-carbon of the double bond. It can be supposed that the distribution of positive charge is not even and depends on the stabilisation which can arise from substituents R and R'' /7a/. The open transition state **B** does not preclude nucleophilic assistance to the departing metal, and it is therefore possible that the partial positive charge on tin is also stabilised by electron donation from a solvent or from a nucleophilic moiety of the attacking agent. There are papers reporting on transition states including a solvent molecule to assist in breaking the carbon-tin bond for iododestannylation /5/ and protodestannylation /7a/ of vinylstannanes. However, so far nucleophilic assistance of the anionic moiety has been supposed for the electrophilic cleavage of alkyl /8/, allyl /9/ or aryl /10/ group only but not for the cleavage of vinyl group.



Scheme 2 Mechanism of electrophilic destannylation

It is highly probable that, during decomposition of transition state **B**, the carbon-carbon bond rotates by the shortest path in the direction which allows the stannyl group to stabilise the β-carbocation by hyperconjugation. That leads to rise of the intermediate **C**, which was suggested by Eaborn and coworkers to explain the retention of configuration observed for protodestannylation of trimethylstannylstyrenes /6/. Such intermediates have never been isolated and characterised, but their existence and stability was confirmed by calculations /11/. It might be supposed that employing a strong electrophile allows the latter transition state **B** to approach more the intermediate **C**. On the other hand, in the case of a weak electrophile, an early transition state resembling rather the substrate **A** is formed. The mechanism is finished by rapid decay of intermediate **C** through the transition state **D**, involving cleavage of the tin-carbon bond, and the product **E** with retention of configuration is obtained.

Moreover, it was found that the rate of reaction of vinylstannanes with an electrophile can be considerably affected by substituents on the vinyl group. The substituent on the α-carbon has a largely deactivating effect which was ascribed to steric hindrance (R′ = Me /7/ or Bu /12/) or electron withdrawal (R′ = Ph) /7d/. The exception holds for protodestannylation of some carbomethoxy-substituted vinylstannanes (R′ = CO_2Me), which does not even proceed with retention of configuration, and the alternative allenol mechanism was suggested in this case /7b, 7c/. On the other hand, the substituent on the β-carbon R′′ mostly facilitates electrophilic cleavage of the vinyl group by stabilisation of the partial positive charge existing on the carbon remote to tin in the transition state B /5-7/. For vinylstannanes substituted on the β-carbon by a Lewis-basic heteroatom (O, S, N), it was moreover proved that the conjugation of lone electron pairs with π-orbitals of the double bond causes increasing of electron density on the α-carbon. Therefore, an electrophile preferably attacks the α-carbon instead of the Lewis-basic heteroatom, and remarkably fast electrophilic demetallation takes place instead of heterolytic fragmentation reaction /12, 13/. On the contrary, an electron-withdrawing carbomethoxy group on the carbon remote to tin hinders cleavage of the vinyl group /7b, 7c/.

In addition, for 2-functionalised vinylstannanes, the difference in reactivity of *E*- and *Z*-isomers has been reported by several authors. In most cases, the *E*-isomer undergoes electrophilic substitution faster than the corresponding *Z*-isomer, whereas the difference is markedly dependent on the nature of the substituent. If the substituent is methyl or phenyl, only an insignificant difference was observed in the case of reactions with HCl in methanol containing 5% of water (k_E/k_Z = 1.4 and 1.1, respectively) /7/. However, *E*-isomers of 2-carbomethoxy- /7b, 7c/ and 2-ethoxy- or 2-ethylthio- /12/ substituted vinylstannanes undergo protodestannylation about 4 and 10 times faster than the corresponding *Z*-isomer, respectively. Moreover, it seems that the difference in reactivity of stereoisomers is also dependent on the nature of electrophile, because the ratio k_E/k_Z obtained in the case of protodestannylation of 2-methyl-substituted vinylstannanes is smaller than that obtained in the case of iododestannylation (k_E/k_Z = 1.4 and 3.8, respectively) /5/. Moreover, the reversed relative order of reactivity (k_E/k_Z = 0.9) was observed for protodestannylation of trimethyl(styryl)stannanes in acetic acid/methanol system.

Although a number of papers reporting on this observation have been published, no satisfactory explanation has yet been offered. Therefore, the set of vinylstannanes of general formula (*E*)/(*Z*)-$R_3SnC(R')=CHR''$ (Scheme 3) was prepared and the kinetics of reactions with acetic, chloroacetic and trifluoroacetic acid in $CDCl_3$ at 25°C were studied by means of ^1H NMR spectroscopy.

2. MATERIALS AND METHODS

2.1. General Information

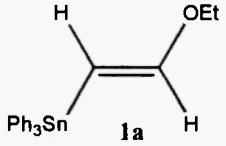
The syntheses were carried out under argon using standard Schlenk techniques. Diethyl ether and THF were distilled from sodium benzophenone ketyl. Hexane was dried over $LiAlH_4$ and distilled prior to use. Dibutyldichlorostannane, tributylchlorostannane, tributylstannane, *n*-butyllithium, 1,2-dibromoethane, ethynylbenzene, hex-1-yne, 3,3-dimethylbut-1-yne, AIBN, 1-(2-bromovinyl)benzene were obtained from Sigma-Aldrich or Fluka. Dibutylstannane /14/, ethoxyethyne /15/, 1-bromohex-1-ene /16/, bromoethene /17/, (*E*)-1-bromo-1,2-diethoxyethene /18/ were prepared in accordance with procedures described in the literature.

^1H, ^{13}C and ^{119}Sn NMR spectra were recorded using a 5mm tuneable probehead on a Bruker AMX 360 (^1H: 360.13 MHz, ^{13}C: 90.57 MHz, ^{119}Sn: 134.29 MHz) and a Bruker AVANCE 500 (^1H: 500.13 MHz, ^{13}C: 125.77 MHz, ^{119}Sn: 186.48 MHz) spectrometer in $CDCl_3$ at 295 K. ^1H and ^{13}C and ^{119}Sn chemical shifts are given in ppm with respect to Me_4Si and Me_4Sn, respectively, and coupling constants *J* in Hz. The gradient-assisted 2D spectra (^1H,^{13}C-HSQC; ^1H,^{119}Sn-HMQC /19/) were recorded using a 5mm tuneable inverse probehead with Z-gradient shielding on Bruker AVANCE 500 spectrometer.

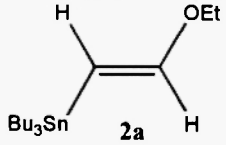
2.2. Syntheses and characterisation of vinylstannanes

The syntheses and characterisation of ((E/Z)-2-ethoxyvinyl)triphenylstannane (**1a/1b**) and tributyl((E/Z)-2-ethoxyvinyl)stannanes (**2a/2b**) were described elsewhere /12,13/. Tributylvinylstannane (**8**) was prepared from bromoethene and tributylchlorostannane by the Grignard method /20/.

E-isomers



trifenyl((*E*)-2-ethoxyvinyl)stannane



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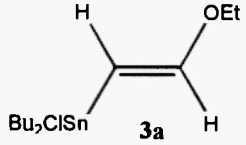
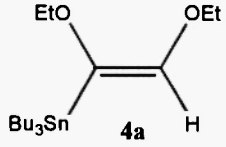
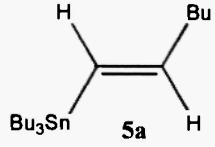


dibutylchloro((*E*)-2-ethoxyvinyl)stannane



tributyl((*E*)-1,2-diethoxyvinyl)stannane



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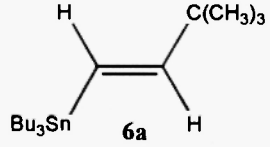

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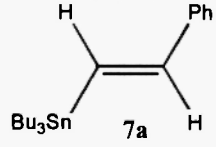
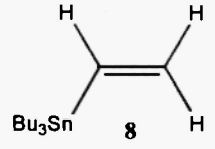
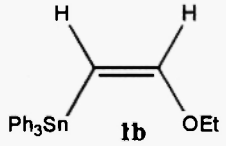


tributyl((*E*)-styryl)stannane

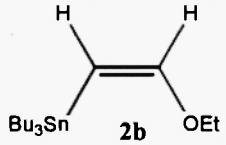


Tributylvinylstannane

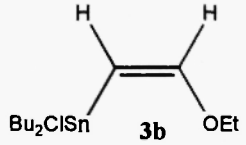
Z-isomers



trifenyl((*Z*)-2-ethoxyvinyl)stannane



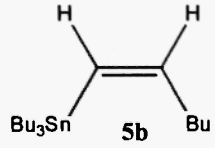
tributyl((*Z*)-2-ethoxyvinyl)stannane



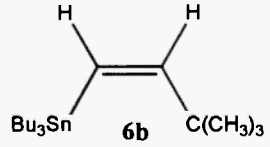
dibutylchloro((*Z*)-2-ethoxyvinyl)stannane

Not prepared

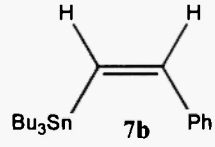
4b



tributyl((*Z*)-hex-1-enyl)stannane



tributyl((*Z*)-3,3-dimethylbut-1-enyl)stannane



tributyl((*Z*)-styryl)stannane

Scheme 3 Vinylstannanes under study

2.2.1. Dibutylchloro((E/Z)-2-ethoxyvinyl)stannane (3a/3b)

Dibutyldichlorostannane (7.8 mmol, 2.38 g) in THF (10 ml) was added to dibutylstannane (7.8 mmol, 1.84 g). After stirring for 30 min at room temperature, the mixture was cooled to 0 °C. Then ethoxyethyne (15.6 mmol, 1.1g) was added dropwise and the mixture was stirred for 15 min at 0 °C and 1 h at room temperature. After removing of the solvent on a rotary evaporator, brown oil was obtained consisting of primarily *Z*-isomer **3b** (purity 95%). The vacuum distillation (b.p. 84-86°C/3.10^{2} Torr) afforded colourless oil (3.4 g, yield 64.2%) containing 32% of **3a** and 68% of **3b**.

3a: ^{1}H NMR: δ = 6.50 (d, 1H, $^{3}J_{HH}$ = 15.6, $^{3}J_{SnH}$ = 50.0, SnCH=C<u>H</u>), 4.79 (d, 1H, $^{3}J_{HH}$ = 15.6, $^{2}J_{SnH}$ = 65, SnC<u>H</u>=CH), 3.84 (q, 2H, $^{3}J_{HH}$ = 7.1, OC<u>H</u>$_2$CH$_3$), 1.64 (m, 4H, SnC<u>H</u>$_2$CH$_2$), 1.38-1.34 (m, 8H, CH$_2$(C<u>H</u>$_2$)$_2$CH$_3$), 1.29 (t, 3H, OCH$_2$C<u>H</u>$_3$), 0.92-0.89 (t, 6H, (CH$_2$)$_3$C<u>H</u>$_3$). ^{13}C NMR: δ = 158.0 ($^{2}J_{SnC}$ = 66.7, SnCH=<u>C</u>H), 93.7 ($^{1}J_{SnC}$ = 468.2, Sn<u>C</u>H=CH), 63.5 (O<u>C</u>H$_2$CH$_3$), 27.6 ($^{2}J_{SnC}$ = 25, SnCH$_2$<u>C</u>H$_2$), 26.6 ($^{3}J_{SnC}$ = 68.8, CH$_2$<u>C</u>H$_2$CH$_3$), 17.8 ($^{1}J_{SnC}$ = 405.4, Sn<u>C</u>H$_2$CH$_2$), 14.4 (OCH$_2$<u>C</u>H$_3$), 13.5 ((CH$_2$)$_3$<u>C</u>H$_3$). ^{119}Sn NMR: δ = 108,1.

3b: ^{1}H NMR: δ = 6.84 (d, 1H, $^{3}J_{HH}$ = 6.5, $^{3}J_{SnH}$ = 133.4, SnCH=C<u>H</u>), 4.81 (d, 1H, $^{3}J_{HH}$ = 6.5, $^{2}J_{SnH}$ = 60, SnC<u>H</u>=CH), 3.84 (q, 2H, $^{3}J_{HH}$ = 7.1, OC<u>H</u>$_2$CH$_3$), 1.65 (m, 4H, SnC<u>H</u>$_2$CH$_2$), 1.38-1.34 (m, 8H, CH$_2$(C<u>H</u>$_2$)$_2$CH$_3$), 1.23 (t, 3H, OCH$_2$C<u>H</u>$_3$), 0.92-0.89 (m, 6H, (CH$_2$)$_3$C<u>H</u>$_3$). ^{13}C NMR: δ = 157.6 ($^{2}J_{SnC}$ = 15.8, SnCH=<u>C</u>H), 99.8 ($^{1}J_{SnC}$ = 447.3, Sn<u>C</u>H=CH), 67.5 (O<u>C</u>H$_2$CH$_3$), 27.6 ($^{2}J_{SnC}$ = 25, SnCH$_2$<u>C</u>H$_2$), 26.5 ($^{3}J_{SnC}$ = 72.5; CH$_2$<u>C</u>H$_2$CH$_3$), 18.7 ($^{1}J_{SnC}$ = 403.1, Sn<u>C</u>H$_2$CH$_2$), 15.2 (OCH$_2$<u>C</u>H$_3$), 13.5 ((CH$_2$)$_3$<u>C</u>H$_3$). ^{119}Sn NMR: δ = 92.9.

2.2.2. Tributyl((E)-1,2-diethoxyvinyl)stannane (4a)

A solution of *n*-butyllithium in hexane (26 mmol, 16 ml, 1.628 M) was added dropwise to (*E*)-1-bromo-1,2-diethoxyethene (26 mmol, 5.07 g) in THF (25 ml) at -78 °C. After 30 min of stirring, tributylchlorostannane (26 mmol, 8.46 g) was added. Afterwards, the reaction mixture was warmed up to room temperature and water (50 ml) was added. The obtained mixture was extracted with Et$_2$O (2x50 ml). The extract was dried over anhydrous Na$_2$SO$_4$ and solvents were removed by rotary evaporation. The residue was distilled at 5·10^{-3} Torr and **4a** (7.8 g, yield 74 %) was obtained as colourless oil boiling at 78-80 °C.

^{1}H NMR: δ = 5.14 (s, 1H, $^{3}J_{SnH}$ = 11.8, SnC(OEt)=C<u>H</u>), 3.79 (q, 2H, $^{3}J_{HH}$ = 7.1, OC<u>H</u>$_2$CH$_3$), 3.73 (q, 2H, $^{3}J_{HH}$ = 7.0, OC<u>H</u>$_2$CH$_3$), 1.51 (m, 6H, SnCH$_2$C<u>H</u>$_2$), 1.32 (m, 6H, CH$_2$C<u>H</u>$_2$CH$_3$), 1.26 (t, 3H, OCH$_2$C<u>H</u>$_3$), 1.25 (t, 3H, OCH$_2$C<u>H</u>$_3$), 0.92 (m, 6H, SnC<u>H</u>$_2$CH$_2$), 0.88 (t, 9H; (CH$_2$)$_3$C<u>H</u>$_3$). ^{13}C NMR: δ = 141.4 ($^{1}J_{SnC}$ = 427.0, SnC(OEt)=CH), 137.6 ($^{2}J_{SnC}$ = 126.6, SnC(OEt)=<u>C</u>H), 68.2 (O<u>C</u>H$_2$CH$_3$), 67.8 (O<u>C</u>H$_2$CH$_3$), 28.9 ($^{2}J_{SnC}$ = 19.9, SnCH$_2$<u>C</u>H$_2$), 27.2 ($^{3}J_{SnC}$ = 59.1, CH$_2$<u>C</u>H$_2$CH$_3$), 15.5 (OCH$_2$<u>C</u>H$_3$), 15.1 (OCH$_2$CH$_3$), 13.5 ((CH$_2$)$_3$<u>C</u>H$_3$), 10.6 ($^{1}J_{SnC}$ = 342.9, Sn<u>C</u>H$_2$CH$_2$). ^{119}Sn NMR: δ = -47.4.

2.2.3. Tributy((E/Z)-hex-1-enyl)stannane (5a/5b)

A mixture of Et$_2$O (20 ml) and THF (10 ml) with a catalytic amount of 1,2-dibromoethane was added to magnesium chips (90 mmol, 2.2g) previously activated by iodide vapours. Then 1-bromohex-1-ene (18.4 mmol, 3g) in THF (10 ml) was added with stirring and the reaction was refluxed for 20 h. After cooling to room temperature, tributylchlorostannane was added and the reaction mixture was refluxed for additional 3 h.

Afterwards saturated solution of NH_4Cl (60 ml) and Et_2O (100 ml) was added. The organic layer was separated, washed with two portions of water (50 ml), dried over anhydrous Na_2SO_4 and the solvents were removed on a rotary evaporator. The crude product was purified by vacuum distillation at $5.25 \cdot 10^{-3}$. The fraction boiling at 75-76 °C (2.8g, yield 41 %) consisted of **4a** (29 %) and **4b** (71 %).

5a: ^{1}H NMR: δ = 5.96 (dt, 1H, $^3J_{HH}$ = 18.9, $^3J_{HH}$ = 5.9, $^3J_{SnH}$ = 66.7, SnCH=C<u>H</u>), 5.87 (d, 1H, $^3J_{HH}$ = 18.9, $^2J_{SnH}$ = 80.7, SnC<u>H</u>=CH), 2.14 (m, 2H, CH=CHC<u>H</u>$_2$), 0.8-1.5 (m, 34H, remaining (C<u>H</u>$_2$)$_3$C<u>H</u>$_3$). ^{13}C NMR: δ = 149.8 (SnCH=<u>C</u>H), 126.9 (Sn<u>C</u>H=CH, $^1J_{SnC}$ = 340.9), 37.6 ($^3J_{SnC}$ = 61.9, CH=CH<u>C</u>H$_2$), 31.1 (=CHCH$_2$<u>C</u>H$_2$), 29.1 ($^2J_{SnC}$ = 20.3, SnCH$_2$<u>C</u>H$_2$), 27.3 ($^3J_{SnC}$ = 53.0, Sn(CH$_2$)$_2$<u>C</u>H$_2$), 22.2 (=CH(CH$_2$)$_2$<u>C</u>H$_2$), 14.0 (Sn(CH$_2$)$_3$<u>C</u>H$_3$)$_3$), 11.0 (=CH(CH$_2$)$_2$ <u>C</u>H$_3$), 9.4 ($^1J_{SnC}$ = 340.6, Sn<u>C</u>H$_2$CH$_2$). ^{119}Sn NMR: δ = -50.0.

5b: ^{1}H NMR: δ = 6.53 (dt, 1H, $^3J_{HH}$ = 12.4, $^3J_{HH}$ = 7.0, $^3J_{SnH}$ = 145.4, SnCH=C<u>H</u>), 5.79 (d, 1H, $^3J_{HH}$ = 12.4, $^2J_{SnH}$ = 74.8, SnC<u>H</u>=CH), 2.03 (m, 2H, =CHC<u>H</u>$_2$CH$_2$), 0.8-1.5 (m, 34H, remaining (C<u>H</u>$_2$)$_3$C<u>H</u>$_3$). ^{13}C NMR: δ = 149.3 (SnCH=<u>C</u>H), 127.6 ($^1J_{SnC}$ = 391.5, Sn<u>C</u>H=CH), 36.9 ($^3J_{SnC}$ = 38.2, =CH<u>C</u>H$_2$CH$_2$), 32.1 (=CHCH$_2$<u>C</u>H$_2$), 29.2 ($^2J_{SnC}$ = 20.3, SnCH$_2$<u>C</u>H$_2$), 27.3 ($^3J_{SnC}$ = 55.6, Sn(CH$_2$)$_2$<u>C</u>H$_2$CH$_3$), 22.5 (=CH(CH$_2$)$_2$<u>C</u>H$_2$CH$_3$), 14.0 (=CH(CH$_2$)$_2$<u>C</u>H$_3$), 13.7 (Sn(CH$_2$)$_3$<u>C</u>H$_3$), 10.2 ($^1J_{SnC}$ = 338.6, Sn<u>C</u>H$_2$CH$_2$). ^{119}Sn NMR: δ = -60.3.

2.2.4. Tributyl((E)-3,3-dimethylbut-1-enyl)stannane (6a)

Tributylstannane (15 mmol, 4.37 g) was added dropwise to a solution of 3,3-dimethylbut-1-yne (15 mmol, 1.23 g) and $Pd(PPh_3)_4$ (0.15 mmol, 170 mg) in THF (10 ml) at 0 °C in the dark. After 30 min of stirring, the reaction mixture was warmed to room temperature and stirred for additional 1h. After removing the solvent on a rotary evaporator, the residue was purified by rapid column chromatography on silicagel, eluting with hexane. Hexane was removed on a rotary evaporator. The resulting oil was distilled under reduced pressure (60-61 °C/$1 \cdot 10^{-2}$ Torr), yielding 4.1 g (73.2 %) of **6a**.

^{1}H NMR: δ = 5.97 (d, 1H, $^3J_{HH}$ = 19.3, $^3J_{SnH}$ = 70.6, SnCH=CH), 5.77 (d, 1H, $^3J_{HH}$ = 19.3, $^2J_{SnH}$ = 79.2, SnC<u>H</u>=CH), 1.50 (m, 6H, SnCH$_2$C<u>H</u>$_2$), 1.32 (m, 6H, CH$_2$C<u>H</u>$_2$CH$_3$), 1.00 (s, 9H, C(C<u>H</u>$_3$)$_3$), 0.89 (t, 9H, (CH$_2$)$_3$C<u>H</u>$_3$), 0.87 (m, 6H, SnC<u>H</u>$_2$CH$_2$). ^{13}C NMR: δ = 160.0 ($^2J_{SnC}$ = 39.7, SnCH=<u>C</u>H), 119.6 ($^1J_{SnC}$ = 403.9, Sn<u>C</u>H=CH), 35.9 ($^3J_{SnC}$ = 56.1, <u>C</u>(CH$_3$)$_3$), 29.2 (C(<u>C</u>H$_3$)$_3$), 29.1 ($^2J_{SnC}$ = 19.9, SnCH$_2$<u>C</u>H$_2$), 27.2 ($^3J_{SnC}$ = 52.8, CH$_2$<u>C</u>H$_2$CH$_3$), 13.7 (CH$_2$)$_2$CH$_3$), 9.4 ($^1J_{SnC}$ = 339.7, Sn<u>C</u>H$_2$CH$_2$). ^{119}Sn NMR: δ = -45.7.

2.2.5. Tributyl((E/Z)-3,3-dimethylbut-1-enyl)stannane (6a/6b)

3,3-Dimethylbut-1-yne (47.5 mmol, 3,9 g) was added to a solution of tributylstannane (9.5 mmol, 2.76 g) and AIBN (0.095 mmol, 16 mg) in hexane (20 ml). The reaction mixture was stirred at 80 °C for 2 h. After removing the solvent on a rotary evaporator, the residue was purified by rapid column chromatography on silicagel, eluting with hexane. Hexane was removed on a rotary evaporator. Vacuum distillation of the resulting oil (58-60 °C/$1 \cdot 10^{-2}$ Torr) afforded 2.5 g (yield 70.6 %) a mixture of **6a** (38 %) and **6b** (62 %).

6b: ^{1}H NMR: δ = 6.64 (d, 1H, $^3J_{HH}$ = 14.0, $^3J_{SnH}$ = 157.7, SnCH=C<u>H</u>), 5.57 (d, 1H, $^3J_{HH}$ = 14.0, $^2J_{SnH}$ = 51.0, SnC<u>H</u>=CH), 1.50 (m, 6H, SnCH$_2$C<u>H</u>$_2$), 1.32 (m, 6H, CH$_2$C<u>H</u>$_2$CH$_3$), 1.03 (s, 9H, C(C<u>H</u>$_3$)$_3$), 0.86-0.93 (m, 15H, SnC<u>H</u>$_2$(CH$_2$)$_2$C<u>H</u>$_3$). ^{13}C NMR: δ = 159.8 (SnCH=<u>C</u>H), 121.6 ($^1J_{SnC}$ = 387.0, Sn<u>C</u>H=CH), 35.3 (<u>C</u>(CH$_3$)$_3$), 29.8 (C(<u>C</u>H$_3$)$_3$), 29.1 ($^2J_{SnC}$ = 19.9, SnCH$_2$<u>C</u>H$_2$), 27.4 ($^3J_{SnC}$ = 58.6, CH$_2$<u>C</u>H$_2$CH$_3$), 13.7

($(CH_2)_2\underline{C}H_3$), 11.8 ($^1J_{SnC}$ = 344.0, $Sn\underline{C}H_2CH_2$). ^{119}Sn NMR: δ = -59.2.

2.2.6. Tributyl((E)-styryl)stannane (7a)

Tributyl((*E*)-styryl)stannane was prepared from 1-(2-bromovinyl)benzene (*E*/*Z* = 85/15, 54.6 mmol, 10 g) and tributylchlorostannane (41.3 mmol, 13.5 g) by the procedure similar to that for **5a**/**5b** (see 2.2.3.). Vacuum distillation of the crude product at $5 \cdot 10^{-3}$ Torr afforded the fraction (10.3 g, yield 48 %) boiling at 119-121 °C, containing 92 % of *E*-isomer **7a** and 8 % of *Z*-isomer **7b**.

^{1}H NMR: δ = 7.48 (d, 2H, *o*-Ph), 7.37 (m, 2H, *m*-Ph), 7,27 (t, 1H, *p*-Ph), 6.93 (m, 2H, $^3J_{SnH}$ = 41.5, $Sn\underline{C}H{=}C\underline{H}$), 1.62 (m, 6H, $SnCH_2C\underline{H}_2$), 1.40 (m, 6H, $CH_2C\underline{H}_2CH_3$), 1.03 (m, 6H, $-Sn\underline{C}H_2CH_2$), 0,96 (t, 9H, $(CH_2)_2C\underline{H}_3$). ^{13}C NMR: δ = 146.0 ($^2J_{SnC}$ = 10.3, $SnCH{=}\underline{C}H$), 129.5 ($^1J_{SnC}$ = 376.9, $Sn\underline{C}H{=}CH$), 138.8 ($^3J_{SnC}$ = 62.1, *i*-Ph), 128.4 (*m*-Ph), 127.5 (*p*-Ph), 126.0 (*o*-Ph), 29.1 ($SnCH_2\underline{C}H_2$), 27.3 ($^3J_{SnC}$ = 54.1, $CH_2\underline{C}H_2CH_3$), 13.7 ($(CH_2)_2\underline{C}H_3$), 9.6 ($^1J_{SnC}$ = 344.7, $Sn\underline{C}H_2CH_2$). ^{119}Sn NMR: δ = -42.9.

2.2.7. Tributyl((E/Z)-styryl)stannane (7a/7b)

The mixture of stereoisomers of tributyl(styryl)stannane was prepared from ethynylbenzene (35 mmol, 3.6g) and tributylstannane (27.5 mmol, 8g) by the procedure similar to that for **6a**/**6b** (see 2.2.5.). Vacuum distillation of the crude product at $5 \cdot 10^{-3}$ Torr afforded the fraction (5.5 g, yield 51 %) boiling at 108-111 °C containing 55 % of *E*-isomer **7a** and 45 % of *Z*-isomer **7b**.

7b: ^{1}H NMR: δ = 7.68 (d, 1H, $^3J_{HH}$ = 13.7, $^3J_{SnH}$ = 137.1, $SnCH{=}C\underline{H}$), 7.48 (d, 2H, *o*-Ph), 7,37 (t, 2H, *m*-Ph), 7.32 (t, 1H, *p*-Ph), 6.25 (d, 1H, $^3J_{HH}$ = 13.7, $^2J_{SnH}$ = 57.6, $Sn\underline{C}H{=}CH$), 1.62 (m, 6H, $SnCH_2C\underline{H}_2$), 1.30 (m, 6H, $CH_2C\underline{H}_2CH_3$), 1.03 (t, 6H, $Sn\underline{C}H_2CH_2$), 0.90 (t, 9H, $(CH_2)_3C\underline{H}_3$). ^{13}C NMR: δ = 147.4 ($^2J_{SnC}$ = 7.3, $SnCH{=}\underline{C}H$), 132.8 ($^1J_{SnC}$ = 358.3, $Sn\underline{C}H{=}CH$), 141.5 ($^3J_{SnC}$ = 27,5; *i*-Ph), 128.1 (*m*-Ph), 127.2 (*p*-Ph), 127.1 (o-Ph), 29.0 ($SnCH_2\underline{C}H_2$), 27.2 ($CH_2\underline{C}H_2CH_3$), 13.7 ($(CH_2)_3\underline{C}H_3$), 10.8 ($^1J_{SnC}$ = 344.4, $Sn\underline{C}H_2CH_2$). ^{119}Sn NMR: δ = -55.7.

2.3. Kinetic studies

2.3.1. Method A

The exact amount of isomerically pure stannane (50 – 100 mg) was weighed into a NMR tube and diluted in $CDCl_3$ (*ca.* 0.5 ml). Then $CHCl_3$ (2 μl) was added as internal standard for integration. In the case of **7a**, HMDS (1 μl) was used instead of $CHCl_3$, whose signal overlaps with signals of stannane. Afterwards the exact amount of CH_3COOH or CD_3COOD (from 1.5 up to 3 equivalents) was added by syringe. The volume of solution was determined from its column depth in the NMR tube. The final concentrations were within the range 0.13 – 0.25 and 0.26 – 0.48 mol.l^{-1} for organotin substrate and acid, respectively. The tube was immediately placed in the thermostated NMR probe at 25°C and ^{1}H NMR spectra at 360 MHz or 500 MHz were recorded at timed intervals. For the reactions of **8**, the NMR tube was thermostated at 25°C outside the NMR probe, since the intervals between measurements were a few days. Each experiment was performed two or three times. From 15 to 20 spectra were obtained in each run and the reaction was followed to 70% of completion at least. The integral intensities of 3 up to 6 signals of vinylic group of the organotin substrate or

the protodestannylation product were evaluated within one experiment. The second order rate constants were obtained from the slopes of linear plots of $\ln(b\text{-}x_t)/(a\text{-}x_t)$ vs. time, where a is starting concentration of tin substrate, b is starting concentration of acetic acid and x_t is conversion in particular time calculated from the integral intensities of selected signals.

2.3.2. Method B

The mixture of stereoisomers (50 – 100 mg) was weighted into a NMR tube and diluted in $CDCl_3$ (*ca.* 0.5 ml). Then $CHCl_3$ (2 µl) was added as internal standard for integration. In the case of mixture **7a**/**7b**, HMDS (1 µl) was used instead of $CHCl_3$. Then ^{1}H NMR spectrum at 360 MHz or 500 MHz was recorded. Afterwards about 2 equivalents of CH_3COOH or CD_3COOD were added by syringe. The tube was immediately placed in the thermostated NMR probe at 25°C and ^{1}H NMR spectra were recorded at timed intervals. In total, about 20 spectra were obtained within two independent experiments. The ratio of second order rate constants k_E/k_Z was obtained using the formula $\ln({}^tI_E/{}^0I_E)/\ln({}^tI_Z/{}^0I_Z)$, where ${}^0I_E$, ${}^tI_E$, ${}^0I_Z$ and ${}^tI_Z$ are integral intensities of selected signal of *E*-isomer and *Z*-isomer obtained in the beginning and in particular time of reaction, respectively /21/.

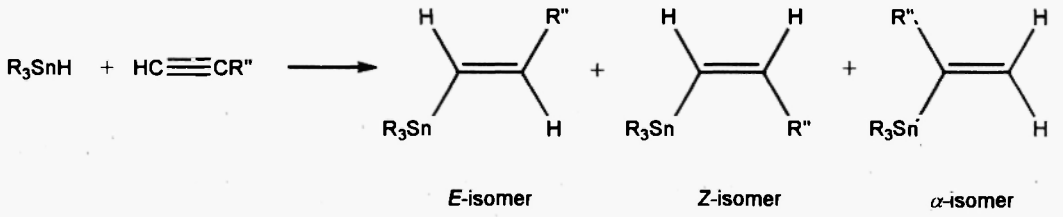
2.3.3. Method C

The mixture of organotin substrates (50 – 100 mg) was weighted into a NMR tube and diluted in $CDCl_3$ (*ca.* 0.5 ml). Then $CHCl_3$ (2 µl) was added as internal standard for integration. In the case of mixture **7a**/**7b**, HMDS (1 µl) was used instead of $CHCl_3$. Then ^{1}H NMR spectrum at 360 MHz or 500 MHz was recorded. Afterwards less then 1/2 equivalent of CH_3COOH, $ClCH_2COOH$ or CF_3COOH was added and ^{1}H NMR spectrum was measured one more time. The experiment was repeated at least 4 times with various amounts of organotin substrates and acids. The ratio of second order rate constants was obtained using the formula described in the previous section (Method B).

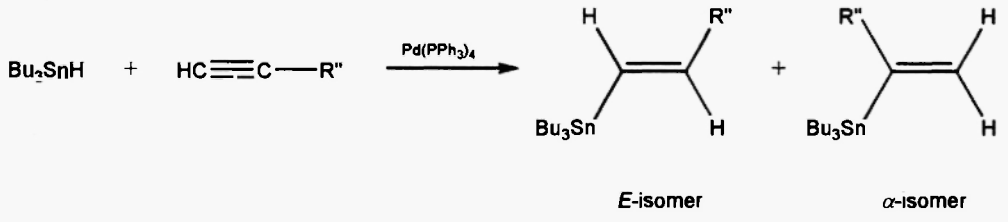
3. RESULTS AND DISCUSSION

3.1. Synthesis and characterisation

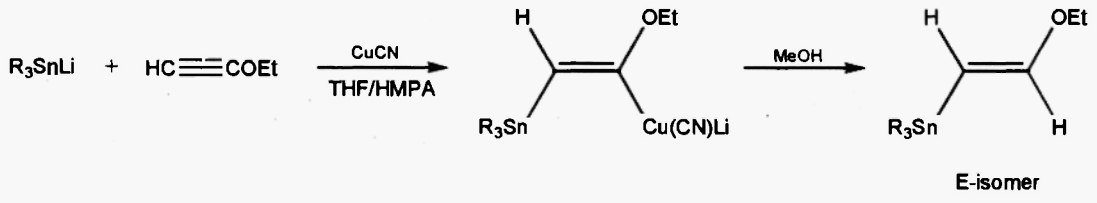
Unlike in previous papers dealing with electrophilic substitution of functionalised vinylstannanes /12/, the method enabling determination of the ratio of rate constants k_E/k_Z is utilised in this study (see 2.3.2. and 2.3.3.), and therefore it was not essential to prepare both stereoisomers in the pure state but only one and their mixture. Nevertheless, four different methods – radical hydrostannylation (Scheme 4) /22/, Pd-catalysed hydrostannylation (Scheme 5) /23/, stannylcupration (Scheme 6) /24/ and coupling of organotin chloride with an appropriate Grignard reagent or vinyllithium compound (Scheme 7) – were used.



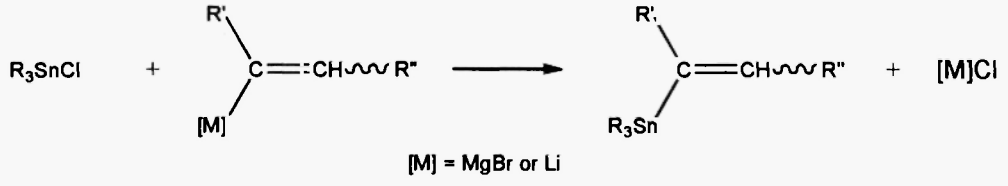
Scheme 4 Radical hydrostannylation



Scheme 5 Pd-catalysed hydrostannylation



Scheme 6 Stannylcupration



Scheme 7 Coupling of organotin chloride with an appropriate Grignard reagent or vinyllithium compound

In the case of 2-ethoxyfunctionalised vinylstannanes, both *E*-isomers (**1a**, **2a**) and *Z*-isomers (**1b**, **2b**) were prepared with sufficiently high stereo- and regioselectivity by stannylcupration (Scheme 6) and radical hydrostannylation (Scheme 4), respectively. In contrast to our previous studies /12, 13/, an excess of 30% of ethoxyethyne was used in the case of radical hydrostannylations, which brings about higher selectivity, and therefore *Z*-isomers (**1b**, **2b**) were isolated with purity of about 95 %. Radical hydrostannylation (Scheme 4) was also successfully used for preparation of dibutylchloro-(2-ethoxyvinyl)stannanes (**3a**/**3b**) whereas dibutylchlorostannane prepared in situ from dibutylstannane and dibutyldichlorostannane was used /25/. The crude product consists of primarily *Z*-isomer (purity about 95 %), but the mixture of stereoisomers containing 32% of *E*-isomer (**3a**) and 68% of *Z*-isomer (**3b**) was obtained after vacuum distillation. Thus, it seems that *Z*-isomer, as the kinetically controlled product, can easily undergo isomerisation catalysed by organotin

radicals to the thermodynamically more stable *E*-isomer /22/.

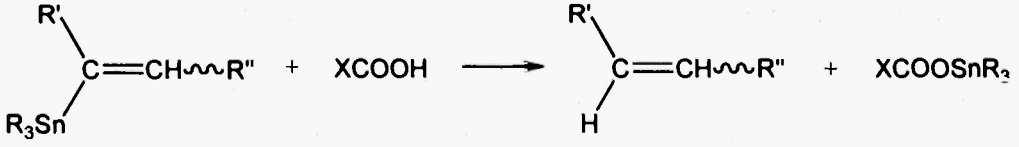
The attempts to prepare 1,2-diethoxyfunctionalised vinylstannes (**4**) by hydrostannylation and stannylcupration methods failed due to very low stability of the starting diethoxyethyne. Therefore, *E*-isomer (**4a**) was prepared by coupling of tributylchlorostannane with (*E*)-1,2-diethoxyvinyllithium which was prepared in situ from *n*-butyllithium and (*E*)-1-bromo-1,2-diethoxyethene (Scheme 7) /26/. The corresponding *Z*-isomer (**4b**) was not prepared due to inaccessibility of (*Z*)-1-bromo-1,2-diethoxyethene. The analogous reaction, i.e. the reaction of tributylchlorostannane with the Grignard reagent of the appropriate vinylbromide, was also used for preparation of tributy((*E*/*Z*)-hex-1-enyl)- (**5a**/**5b**) and tributy((*E*)-styryl)stannane (**7a**). In the former case, the mixture of isomers of 1-bromohex-1-ene was used as starting material and the mixture of isomers **5a**/**5b** was therefore obtained as product. However, for preparation of **7a**, almost pure 1-((*E*)-2-bromovinyl)benzene (85 %) was used and remains of *Z*-isomer **7b** were removed from the crude product by vacuum distillation. For both reactions, no isomerisation was observed.

In the case of t-butyl- (**6a**/**6b**) and phenyl-substituted (**7a**/**7b**) vinylstannanes, the mixtures of stereoisomers were obtained by radical hydrostannylation of 3,3-dimethylbut-1-yne and ethynylbenzene (Scheme 4), respectively. Both reactions showed good regioselectivity and no α-isomers were yielded. However, stereoselectivity was rather poor and the products contained about 38 % and 55 % of *E*-isomer, respectively. Tributyl((*E*)-3,3-dimethylbut-1-enyl)stannane (**6a**) was prepared in an isomerically pure state by Pd-catalysed hydrostannylation (Scheme 5) which proceeds with unusually good regioselectivity and does not afford any α-isomer, likely due to sterical hindrance of the bulky *t*-butyl group.

All prepared vinylstannanes were fully characterised by ^{1}H, ^{13}C and ^{119}Sn NMR spectra. Obtained parameters are given in the Experimental section (see 2.2.). Chemical shifts of α-carbon of double bond, which will be used in further discussion, are summarised in Table 3. The assignment of the configurational geometry of substituents on vinyl group using the relative magnitudes of $^{3}J(^{1}H,^{1}H)$ and $^{n}J(^{119}Sn,^{1}H)$ was already described elsewhere /12/. To assign ^{13}C resonances, the values of $^{n}J(^{119}Sn,^{13}C)$ were used. In particular cases, $^{1}H,^{13}C$-HSQC spectra were also utilised. In mixtures of isomers, ^{117}Sn resonances were assigned by means of 2D $^{1}H,^{119}Sn$-HMQC spectra.

3.2. Kinetic studies

Reactions of vinylstannanes with carboxylic acids XCOOH (X = CH_3, $ClCH_2$ and CF_3) in $CDCl_3$ at 25°C were studied by means of ^{1}H NMR spectroscopy. In all cases, it was found that protodestannylation reaction takes places selectively in accordance with Scheme 8 and no side reactions were observed.



Scheme 8 Reaction of vinylstannane with carboxylic acid

Compounds obtained in an isomerically pure state (**1a**, **1b**, **2a**, **2b**, **3b**, **6a**, and **7a**) were also treated with CH_3COOD, whereas the integral intensities of vinyl protons on the carbon remote to substituent R'' proved that protodestannylation proceeds with retention of configuration at the carbon-carbon double bond. For reactions of **1a**, **1b**, **6a**, **7a** and **8** with CH_3COOH and CH_3COOD, it was found that the rate equation is strictly second order, first order in each reactant, and the second order rate constants were evaluated by method A (see 2.3.1.). Obtained rate constants along with k_H/k_D values are listed in Table 1.

Table 1

The second order rate constants for reactions of vinylstannanes with CH_3COOH and CH_3COOD in $CDCl_3$ at 25°C and k_H/k_D values.

	k[min^{-1}mol^{-1}l]		k_H/k_D
	CH_3COOH	CH_3COOD	
1a	$(4.10 \pm 0.24) \cdot 10^{-1}$ [a]	$(5.50 \pm 0.70) \cdot 10^{-2}$	7.5
1b	$(4.39 \pm 0.44) \cdot 10^{-2}$ [a]	$(8.39 \pm 0.96) \cdot 10^{-3}$	5.2
6a	$(4.96 \pm 0.28) \cdot 10^{-3}$	$(1.27 \pm 0.06) \cdot 10^{-3}$	3.9
7a	$(7.64 \pm 1.39) \cdot 10^{-3}$	$(1.17 \pm 0.24) \cdot 10^{-3}$	6.5
8	$(5.44 \pm 0.37) \cdot 10^{-5}$	[b]	> 1

[a] Reference 12, [b] Conversion less 30% was achieved after 40 days. Measurement not finished.

The reactions with acids of the remaining compounds obtained in isomerically pure state (**2a**, **2b**, **3b** and **4a**) were so fast that it was impossible to follow their courses by NMR spectroscopy and it was impossible to determine the rate constants. Mixtures **1b**/**2b**, **2b**/**3b** and **2a**/**4a** were therefore investigated by method C (see 2.3.3.). Since the differences in reactivity were too large, it was determined only qualitatively that the order of reactivity for reactions of 2-ethoxyfunctionalised vinylstannanes with acetic acid is Ph_3Sn (**1b**) < Bu_3Sn (**2b**) < Bu_2SnCl (**3b**) /27/. Moreover, it was found that **3b** is reactive in so far that it slowly undergoes protodestannylation even when being in contact with moisture. On the other hand, trifluoroacetic acid reacts with dibutylchlorostannyl derivative **3b** slower (by a factor 2.31 ± 0.83) than with tributylstannyl derivative **2b**. Furthermore, it was found that 2-ethoxy functionalised vinylstannane **2a** reacts with acetic acid faster (by a factor 4.4 ± 0.52) than 1,2-diethoxyfunctionalised vinylstannane **4a**.

In the case of compounds for which neither isomer was obtained in isomerically pure state, or where the second order rate constants were not obtained due to the very fast protodestannylation reactions, the ratios of rate constants k_E/k_Z were acquired using methods B and C (see 2.3.2. and 2.3.3.), respectively. Obtained values k_E/k_Z along with that calculated from the second order rate constants are summarised in Table 2.

It is obvious that 2-ethoxyfunctionalised vinylstannanes react with acetic acid significantly faster than the rest of vinylstannanes under study, which is in accordance with the proposed mechanism of protodestannylation. The ethoxy group on the vinyl carbon remote to tin facilitates the rate determining attack of electrophile because it increases the electron density on the α-carbon atom of the double bond, as evident from the values of $\delta(^{13}C)$, which are significantly shifted upfield with respect to **8** (Table 3) /28/, and

simultaneously stabilises the partial positive charge existing on the β-carbon atom of the double bond in the transition state /12/. On the other hand, the values of ^{13}C chemical shift denote that the ethoxy group on the vinyl carbon proximate to tin decreases the electron density on the α-carbon atom (Table 3), and this is probably the cause of the above mentioned lower reactivity of 1,2-diethoxyfunctionalised vinylstannane **4a** compared to 2-ethoxyfunctionalised vinylstannane **2a**. However, considering that butyl /12/ or methyl /5, 7/ substituent on the α-carbon has a parallel effect, a steric hindrance of α-ethoxy group cannot be entirely excluded. Nevertheless, **4a** reacts with acetic acid significantly faster than tributylvinylstannane **8**, though ^{13}C chemical shifts indicate that the electron density on the α-carbon of **4a** is slightly lower (Table 3). Thus, it seems that the ethoxy group on the vinyl carbon remote to tin facilitates protodestannylation by stabilisation of the transition state positive charge at the carbon to which it is attached, rather than by increasing electron density on the other vinyl carbon.

Table 2

The values of k_E/k_Z obtained for reactions of functionalised vinylstannanes with CH_3COOH, $ClCH_2COOH$ or CF_3COOH in $CDCl_3$ at 25°C.

	k_E/k_Z		
	CH_3COOH	$ClCH_2COOH$	CF_3COOH
1a/1b	9.3 [a]	-	-
2a/2b	10.49 ± 1.52	3.13 ± 0.16	1.56 ± 0.12
3a/3b	1.04 ± 0.21	-	-
5a/5b	2.06 ± 0.21	-	-
6a/6b	1.51 ± 0.04	-	1.05 ± 0.09
7a/7b	0.51 ± 0.02	-	0.77 ± 0.02

[a] Reference 12.

Table 3

The values of ^{13}C chemical shifts of α-carbon atom of vinyl group in ppm

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
E-isomer (**a**)	89.0	91.5	93.7	141.4	126.9	119.7	129.5	139.2
Z-isomer (**b**)	94.9	97.7	99.8	[a]	127.6	121.6	132.8	

[a] Not prepared

Substitution on the β-carbon by both *t*-butyl (**6a**) and phenyl (**7a**) groups also considerably enhances the reactivity by a factor of about 100 with respect to tributylvinylstannane (**8**), whereas **6a** reacts with acetic acid about 1.5 times slower than **7a** (Table 1), although according to ^{13}C chemical shift **6a** has higher electron density on the α-carbon (Table 3). An analogous phenomenon was also observed for $Ph_3SnC(Ph)=CHNMe_2$, which undergoes protodestannylation significantly faster than **1a** though $\delta(^{13}C^{\alpha})$ of **1a** is shifted 25 ppm

upfield /12/. Taking into account that phenyl group stabilises a carbocation better than alkyl group and amino group better than alkoxy group /29/, it affirms that stabilisation of partial charge developing at the remote carbon in the transition state is at least as significant for the rate of protodestannylation as the electron density on the carbon-bearing tin group.

In contrast to reactions of phenyl-substituted vinylstannanes with hydrochloric acid in CD_3OD/H_2O /7d/, for reactions of **1a**, **1b**, **6a**, **7a** with acetic acid in $CDCl_3$ significant isotopic effects were discovered (Table 1). This gives evidence about breaking of the H-O bond in the rate determining step and thus it might be assumed that not only the proton, but the whole molecule of acetic acid is involved in the transition state. The higher isotopic effect observed for **7a** (k_H/k_D = 6.5) over **6a** (k_H/k_D = 3.9) denotes that a better proton transfer takes place and consequently more positive charge is localised on the β-carbon and/or tin in the transition state of **7a** than in that of **6a**. It is in accordance with the above-mentioned better capability of phenyl group to stabilise the carbocation in the transition state. Analogously, the values of k_H/k_D obtained for 2-ethoxyfunctionalised vinylstannanes **1a/1b** show that *E*-isomer **1a** adopts the latter transition state with more positive charge stabilised on the β-carbon and/or tin than *Z*-isomer **1b**, which might be related with the difference in reactivity of stereoisomers.

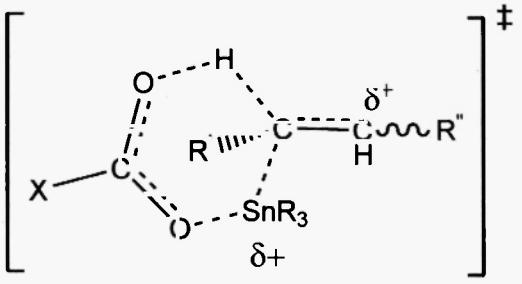
It was shown that triphenylstannyl derivatives (**1a/1b**) react fundamentally slower than tributylstannyl derivatives (**2a/2b**). The same influence of substituents with sp^2 carbon bonded to tin on the rate of electrophilic destannylation was also observed when comparing tetravinylstannane to dialkyldivinylstannane or trialkylvinylstannanes /5,7a/ or triphenylstannyltrimethylstannane to hexamethyldistannane /30/. It was explained that electron donating alkyl groups better stabilise a partial positive charge rising on tin in the transition state than vinyl or aryl groups /5/. However, dibutylchloro(2-ethoxyvinyl)stannanes (**3a/3b**) undergo protodestannylation with weak acids (CH_3COOH, H_2O) very easily, though extremely electron-withdrawing chlorine is bonded to tin. On the other hand, if strong trifluoroacetic acid is used, tributylstannyl derivative **2b** reacts faster than dibutylchlorostannyl derivative **3b**. The analogy can be found in the fact that acetic acid is able to cleave all vinyl groups of tetravinylstannane but trifluoroacetic acid only two /31/. It was suggested that replacing of two vinyl groups by strongly electron withdrawing trifluoroacetic groups hinders the attack of electrophile on the α-carbon so as to disable the cleavage of further vinyl group. The values of ^{13}C chemical shift (Table 3) show that chlorine bonded to tin likewise affects the electron density on α-carbon and consequently **3b** reacts with trifluoroacetic acid slower than **2b**. However, for weak acids it is necessary to take into account also the nucleophilic assistance of the anionic moiety of the attacking acid, which is made easier by electron withdrawing effect of chlorine, in order to explain the reverse order of reactivity.

As can be assumed from the values of ^{13}C chemical shifts, *E*-isomers undergo protodestannylation faster than corresponding *Z*-isomers. The only exception holds for tributyl((*E*)-styryl)stannane (**7a/7b**), which shows the reversed order of reactivity of stereoisomers (k_E/k_Z = 0.51). The ratio of rate constants k_E/k_Z obtained for reaction 2-ethoxyfunctionlised tributylvinylstannnes **2a/2b** with acetic acid is only slightly higher than that of analogous triphenylstannyl derivatives **1a/1b** (Table 2). Thus, it seems that substituents on tin do not significantly affect the difference in reactivity of stereoisomers. In contrast, stereoisomers of dibutylchloro(2-ethoxyvinyl)stannanes (**3a/3b**) show the same reactivity (k_E/k_Z = 1.04). Considering that

Lewis acidity of tin atom in **3a/3b** is higher than in analogous tetraorganotin derivatives (**1a/1b**, **2a/2b**), it seems that the abnormally large difference in the rates of stereoisomers of 2-ethoxyfunctionalised vinylstannanes cannot be caused by O→Sn interaction as suggested by us in a previous paper /12/. Since *n*-butyl (**5a/5b**) and *t*-butyl (**6a/6b**) substituents on the carbon remote to tin cause practically the same difference in reactivity of stereoisomers (k_E/k_Z = 2.06 and 1.51, respectively), the steric hindrance of substituent in *cis*-position and disruption of the solvent cage around the leaving stannyl group, which was supposed by Cochran *et al.* as the reason for lower reactivity of *Z*-isomers, might also be excluded. This opinion is also supported by the fact that tributyl((*E*)-styryl)stannanes (**7a/7b**), with a relatively bulky phenyl substituent on β-carbon, show a reverse order of reactivity.

Moreover, it was proved that the difference in reactivity of stereoisomers is affected by the nature of electrophile (Table 2). While tributyl((*E*)-2-ethoxyvinyl)stannane (**2a**) undergoes protodestannylation with acetic acid in $CDCl_3$ about ten times faster than *Z*-isomer (**2b**), for reactions with chloroacetic acid and trifluoroacetic acid the values of k_E/k_Z 3.13 and 1.56 only were acquired, respectively. Although it is not so apparent as in the previous case, using stronger trifluoroacetic acid instead of acetic acid for protodestannylation of **6a/6b** (R'' = *t*-Bu) and **7a/7b** (R'' = Ph) also diminishes the difference in reactivity of stereoisomers. It also probably explains the fact that for reaction of **7a/7b** with HCl in CD_3OH/H_2O the relative order of reactivity was reversed (k_E/k_Z = 1.1) with respect to reactions with CH_3COOH (see Introduction) /7d/.

Since a significant isotopic effect denotes that the whole molecule of acid is involved in the transition state, it can be supposed that a nucleophilic assistance of the anionic moiety of carboxylic acid takes place similarly to that transition state which was suggested by Winstein and Traylor for acetolysis of dialkylmercury compounds (Scheme 9) /8/.



Scheme 9: Transition state of protodestannylation involving nucleophilic assistance of anionic moiety

Taking into account that tin atom can conjugate with the π-electron system of vinyl group /32/, it might be supposed that mutual *trans*-position of an electron-releasing substituent (OEt or alkyl) and tin centre makes the nuclecleophilic assistance easier than in the case of mutual *cis*-position, while an electron-withdrawing substituent (Ph) has the reverse effect. Taking into consideration this hypothesis and the fact that the nucleophilicity of anionic moiety decreases with the strength of acid, the dependence of the difference in reactivity of stereoisomers on the strength of acid seems to be apparent. It could be also proposed that for strong electrophiles the transition state B is close to the intermediate C (Scheme 2), where

the π-electron system is lapsed, and that diminishes the difference in reactivity. From this viewpoint, the absence of difference in reactivity of stereoisomers observed for dibutylchloro(2-ethoxyvinyl)stannanes (**3a/3b**) can also be explained. In this case, chlorine bonded to tin makes nucleophilic assistance easier so that the effect of substituent on β-carbon atom has no influence.

One could object that *E*-isomers of carbomethoxy-substituted vinylstannanes undergo protodestannylation faster than the corresponding *Z*-isomers though the carbomethoxy group is electron-withdrawing /7b,7c/. However, stabilisation of stannyl group by closing of a five-membered ring, due to coordination of carbonyl oxygen in *cis*-position to tin, can take place in this case. This was already observed for halodestannylation of analogous vinylstannanes, whereas alkyl groups were cleaved preferentially to the vinyl carbon-tin bond, and thus it is highly probable that this effect is stronger than the above discussed one /33/.

4. CONCLUSION

This paper confirms the general mechanism of protodestannylation of vinylstannanes depicted in Scheme 2. It was shown that the stabilisation of positive charge rising at tin and β-carbon in the transition by substituents R and R'', respectively, is as significant for the overall rate of reaction as electron density on the α-carbon of vinyl group. Furthermore, it was suggested that for weak acids, nucleophilic assistance of the anionic moiety to the departing tin atom takes place and this is probably responsible for the difference in reactivity of *E*- and *Z*-isomers. It is supposed that, due to conjugation of tin atom with π-electrons of the vinyl group, mutual *trans*-position of an electron-releasing substituent (OEt or alkyl) and the tin centre makes this nuclecleophilic assistance easier than in the case of mutual *cis*-position, while an electron-withdrawing substituent (Ph) has the reverse effect.

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