ХИМИЯ ГЕТЕРОЦИКЛИЧЕСКИХ СОЕДИНЕНИЙ. — 1999. — № 9. — С. 1185—1196

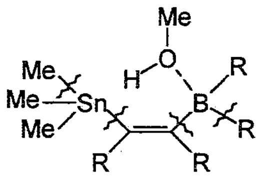
Bernd Wrackmeyer, Gerald Kehr, Sabine Willbold, Roland Boese

NOVEL REARRANGEMENTS AND FORMATION OF 2,5-DIHYDRO-1,2,5-OXONIASTANNABORATOLES VIA METHANOLYSIS OF ZWITTERIONIC η^2-(ALKYN-1-YLBORATE)ALKENYLTIN COMPOUNDS*

Organo-substituted 2,5-dihydro-1,2,5-oxoniastannaboratoles **3** were prepared by methanolysis of zwitterionic η^2-(alkyn-1-ylborate)alkenyltin compounds **1**. Analogously, the bis[η^2-(alkyn-1-yl-borate)alkenyltin derivative **2** reacts with an excess of methanol to give a dimeric MeO-bridged 2,5-dihydro-1,2,5-oxoniastannaboratole **(10a)$_2$**. Various intermediates could be identified by NMR spectroscopy, and the molecular structure of **(10a)$_2$** was determined by X-ray analysis. The structures of several products of the methanolysis indicate that protolysis of an Sn-C= bond occurs first, followed by an MeO/alkenyl exchange reaction.

1. INTRODUCTION

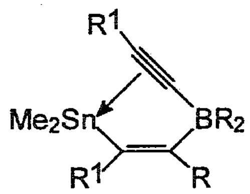
The reaction of organoboron [1–6] or organotin compounds [7–10] with OH acidic reagents provides a preparatively by useful route for the synthesis of hydrocarbons, e.g. in the synthesis of alkenes from the reaction of alkenylboranes or -stannanes with methanol. However, if both dialkylboryl and trialkylstannyl groups are attached to a C=C bond (**A**) a number of less expected products are formed, e.g. as the result of protolysis of an Sn-alkyl bond, rearrangement and/or addition reactions [11] (bonds are indicated that are likely to be attacked by methanol if a more or less weak O-B coordination bond has been formed).



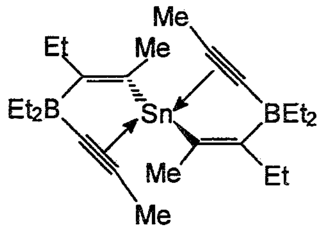
A

This work reports on the reaction of the zwitterionic compounds **1** and **2** with methanol. There are numerous reactive sites in these compounds, even more than in **A**, considering the presence of bridging alkynyl groups and the enhanced Lewis-acidic character of the tin atom in the stannyl group. These compounds **1** [12–17] and **2** [18–20] are intermediates, which could be isolated at low temperature in the course of 1,1-organoboration reactions [21] of bis(alkyn-1-yl)tin and tetrakis(alkyn-1-yl)tin compounds with triorganoboranes .The reactions of **1** and **2** with methanol were studied in a stoichiometric ratio as well as in excess methanol. The reactivity of compound **2** towards less reactive alcohols such as ethanol, isopropanol and *tert*-butanol was also studied. NMR spectroscopic measurements between 208–298 K served for monitoring the progress of the reactions and for the characterisation of the products (^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR). In the case of one of the final reaction products of **2** with methanol, the molecular structure of a novel dimer was determined by X-ray structural analysis.

* Dedicated to A. N. Nesmeyanov 100th birthday.



1



2

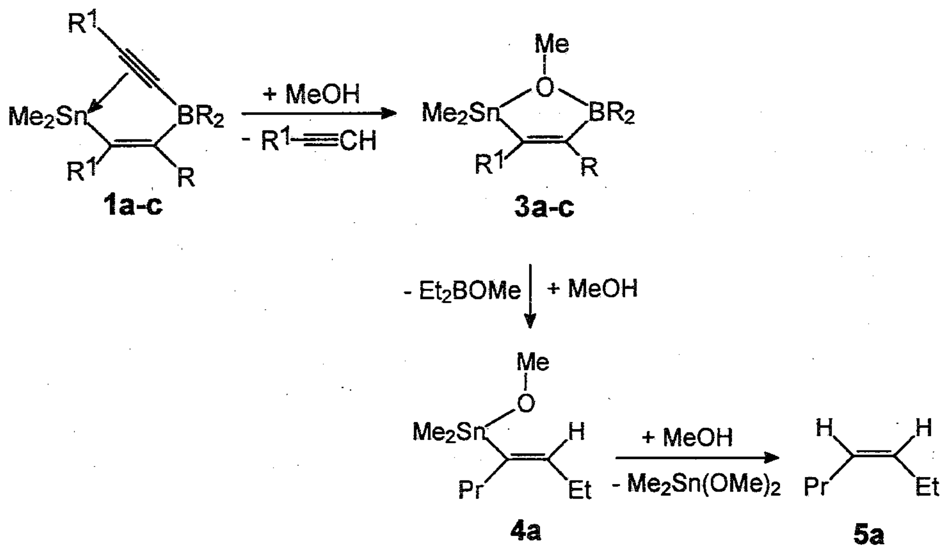
1	a	b	c
R	Et	*i*-Pr	Et
R1	Pr	Et	CH_2NMe_2

2. RESULTS AND DISCUSSION

2.1. Reactions of 1 with methanol

All reactions of **1** with one equivalent of methanol lead to the 2,5-dihydro-2-stanna-1-oxonia-5-boratoles **3**, irrespective of the solvent (THF or hexane), accompanied by elimination of one equivalent of the respective terminal alkyne, as shown in Scheme 1 (the corresponding 2,5-dihydro-1,2,5-oxoniaplumbaboratole is formed if the reaction of **1(Pb)** with MeOH is carried out [18]).The selective formation of the heterocycles **3a** and **3c** is observed at 208 K and 263 K, respectively, whereas **3b** is generated together with **6b** at 298 K. It is known that the bridging alkynyl group can readily move back from the boron to the tin atom. Therefore, a nucleophilic attack of MeOH at the boron atom may shift the alkynyl group to the tin atom (corresponding to an S_N2 mechanism) to give an adduct as shown in **A**, followed by protolysis of the Sn-C≡ bond. Since there is an intramolecular coordinative N-Sn bond in **1c**, this mechanism is more likely than primary nucleophilic attack at the tin atom. In the cases of **1a,b**, the present data do not allow one to distinguish from coordination of MeOH to the formally cationic tin centre in **1** in the first

Scheme 1

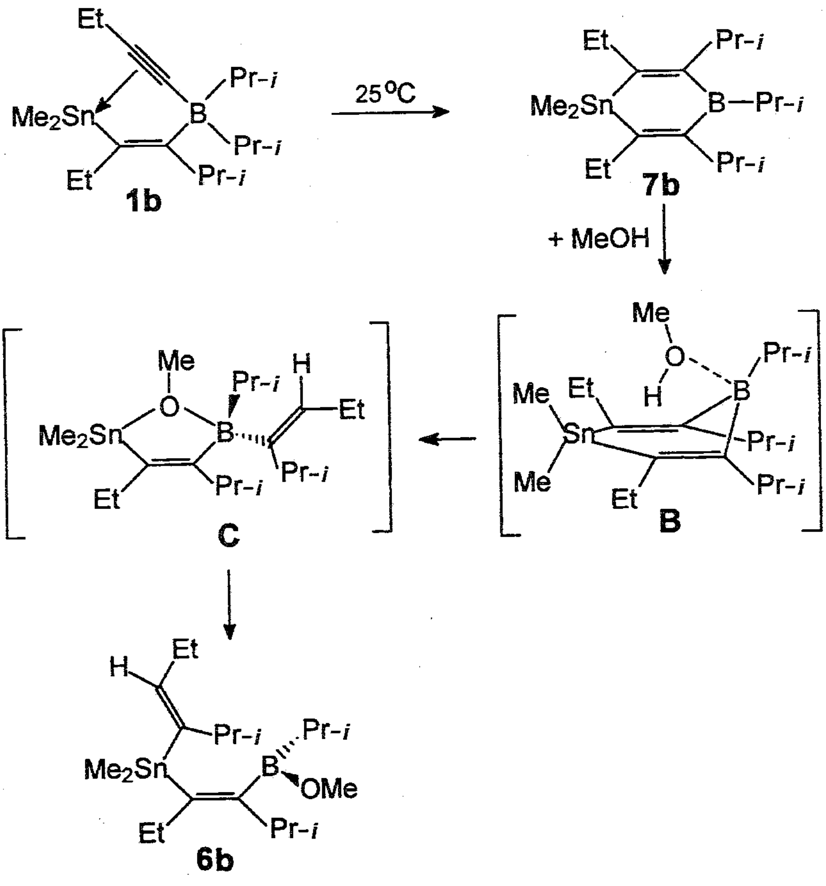


step, followed by elimination of the alkyne in consecutive protolysis and exchange reactions.

Addition of an excess of methanol causes further reactions at room temperature only in the case of **3a**. The first product is **4a** and (*Z*)-hept-3-ene **5a** is the final product (Scheme 1). The compounds **3b** and **3c** are not attacked by an excess of methanol.

The formation of **6b** requires a more detailed explanation (Scheme 2). Since the reaction of **1b** with methanol is slow, it competes with intramolecular 1,1-alkylboration [21]. The latter process leads to the 1,4-stannaboracyclohexa-2,5-diene **7b** [22]. All NMR spectroscopic evidence indicates that **7b** prefers a half-chair conformation [23] in which the boron atom is shifted out of the plane formed by the two C=C units and the tin atom. This conformation facilitates the coordination of methanol to the boron atom in the way shown in **B**, and protolysis of one of the Sn-C= bonds can readily take place.

Scheme 2



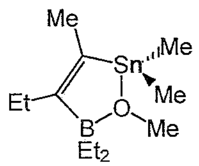
The protolysis of the Sn-C= bond is followed by intramolecular O-B coordination to give the cyclic intermediate **C** (see the compounds **3**). The intermediate **C** can rearrange into **6b** by intramolecular exchange of the alkenyl and the methoxy group. This explains the positions of Et and *i*-Pr in one of alkenyl groups in **6b** which differ from those in **7b**.

2.2. Reaction of 2 with methanol

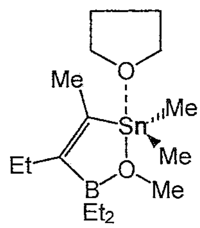
The reaction of the compound **2** with two equivalents of methanol should lead at first, in analogy to the observation in the case of **1**, by elimination of one equivalent of propyne to the 2,5-dihydro-2-stanna-1-oxoniaboratoles **D** and **E**, in which the latter contains the second equivalent of MeOH bonded as a Lewis base. From **E** a second equivalent of propyne can be eliminated, and **8a** is formed by ring closure. The compound **8a** is detected already at 223 K, it is stable only under these mild reaction conditions, and it contains an undefined amount of coordinated methanol. It decomposes when the reaction mixture is warmed to room temperature to give (*Z*)-pent-2-ene, various methoxyboranes and tin methoxides. Alternatively, under less mild reaction conditions (in the presence of an excess of MeOH), a product **9a** is formed which gives **10a**, and finally the dimer **(10a)**$_2$. Thus **8a** could be a precursor of **10a**, and the compounds **8a** and **9a** possess the intermediates **D** and **E** as common precursors.

The comparison of the structures of **8a** and **9a** shows that the positions of Me and Et in one of the alkenyl groups are different. Again it is conceivable that protolysis of an Sn-C= bond occurs first, followed by exchange reactions, as outlined in the case of **6b** (*vide supra*).

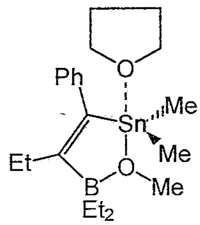
The reaction of **2** with ethanol or 2-propanol gives the compounds analogous to **9a**, and dimerisation is not observed. In the case of *tert*-butanol, the reaction was extremely slow at room temperature, and defined final products could not be identified.



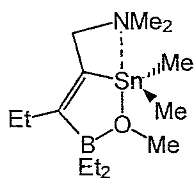
11



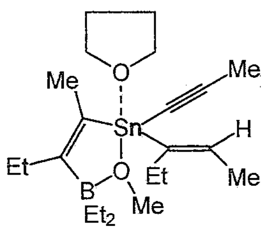
11(THF)



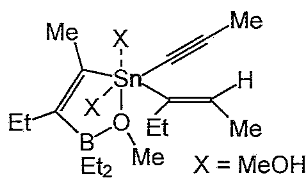
12(THF)



3c



9a(THF)

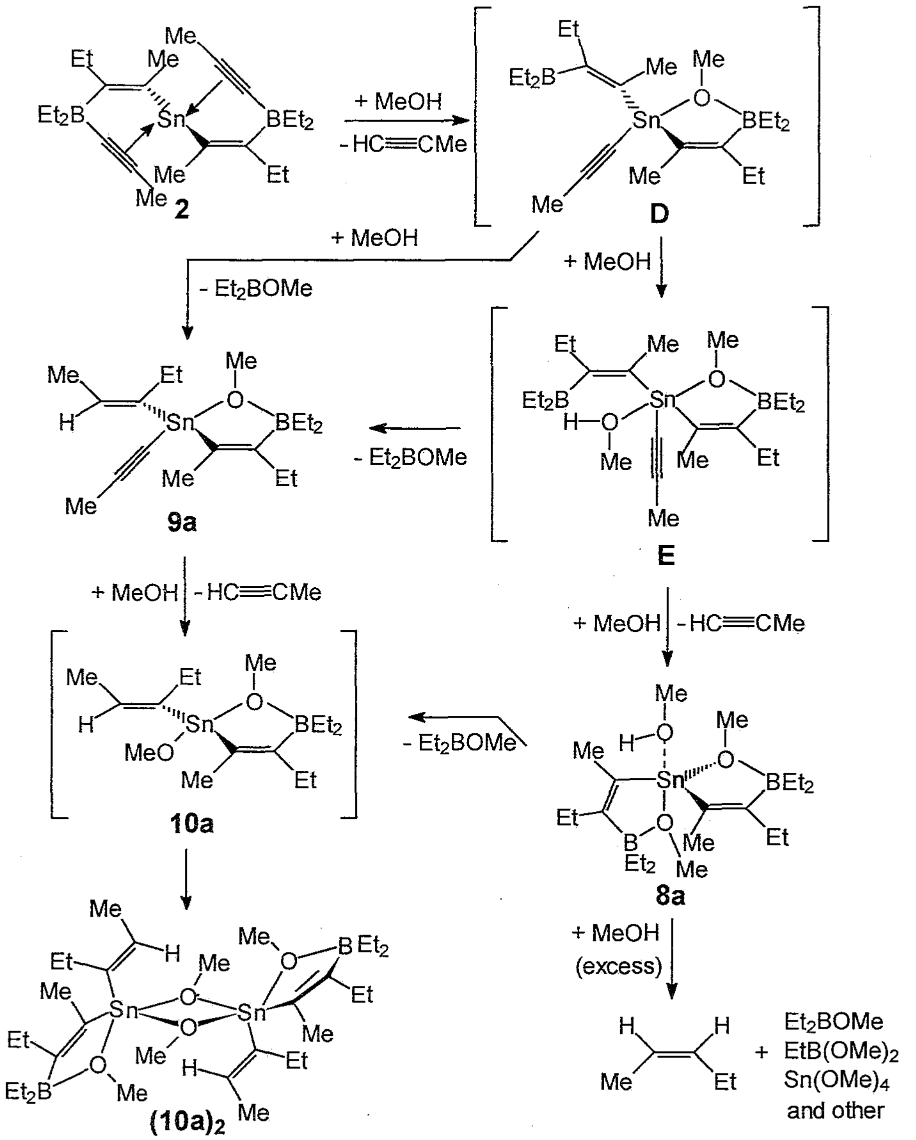


9a(MeOH)

2.3. NMR spectroscopic results

The proposed structures of the products are based on consistent NMR data sets and on data for comparison (Tables 1–5). The ^{1}H NMR spectra are often fairly complex as a result of overlapping signals. However, the position of the proton at the C=C bond (e.g. in **6b** or in **(10a)**$_2$) is clearly indicated by the splitting due to $^3J(^1H,^1H)$. ^{11}B NMR spectra reveal the presence of tri- or tetracoordinate boron atoms. Thus, the δ ^{11}B = +53.0 for **6b** is typical [24,25] of a diorganoboron-oxygen

Scheme 3



compound, and the δ ^{11}B data for **3** and **8**—**12** (δ = 7—9) indicate the coordination number 4 for the boron atoms [24,25]. ^{13}C and ^{119}Sn NMR spectra are conclusive since the $^{117/119}$Sn satellites owing to *J*(Sn,^{13}C) yield valuable structural information, and the δ ^{119}Sn values [26] are also typical of certain structural features. In the ^{13}C NMR spectra, there are also broad signals owing to partially relaxed ^{13}C-^{11}B scalar one-bond coupling [27] which are useful for the assignment. The δ ^{119}Sn value of **6b** (-81.0) is typical of dialkenyltin compounds [26], and δ ^{119}Sn values of **3a,b** (+197.7, 174.3) indicate the neighbourhood of the tin atom to an oxonium-type oxygen [28]. In the case of **3c** (δ ^{19}Sn -23.2), the increase in ^{119}Sn nuclear shielding when compared with that in **3a,b** indicates an intramolecular N-Sn coordination, and this is also evident from the relative increase in the magnitude of $|^{1}J(\mathrm{Sn},^{13}\mathrm{C})|$, as predicted by Bent's model of rehybridisation [29]. Similar effects are always found in the cases of the compounds of type **3** with THF [e.g. **11(THF)** or **12(THF)**] or MeOH, or **8** with MeOH, **9** with THF or MeOH, and in the dimer **(10a)$_2$**

Table 1

^{119}Sn, ^{13}C, ^{11}B NMR data [a] of the 2,5-dihydro-1,2,5-oxoniastannaboratoles 3

No	δ ^{13}C							δ ^{119}Sn
	Me_2Sn	SnC=	BC=	BR_2	R	R^1	OMe	(δ ^{11}B)
3a[b]	-0.7 [277.9]	137.6 [675.8]	175.0 (br)	12.3, 9.8 (br)	25.0, 13.7 [118.8]	34.0, 27.3 [124.3][44.1]	49.0	+197.7 (+10.2)
3b	0.9 [286.6]	139.9 [691.0]	177.3 (br)	16.6, 20.5 (br)	32.4, 21.4 [134.1] [13.6]	27.8, 20.2 [117.7] [n.o.]	51.5	+174.3 (+10.7)
3c	-3.3 [469.2]	127.8 [866.7]	182.1 (br)	12.6, 10.0 (br)	24.8, 14.1 [118.3] [16.3]	61.2, 42.5 [98.1] [n.o.]	47.1	-23.2 (+4.6)

[a] In $CDCl_3$, at 25^{0}C; Coupling constants in Hz: $^nJ(^{119}Sn^{13}C)$ in brackets; n.o.: not observed; (br) denotes broad signals owing to partially relaxed ^{13}C-^{11}B scalar coupling.

[b] δ ^{13}C: 13.3 (CH_3).

Table 2

^{119}Sn, ^{13}C, ^{11}B NMR data [a,b] of the 3-stanna-1,4-pentadiene 6b

No	δ ^{13}C						δ ^{11}B
	Me_2Sn	SnC(Et)=	SnC(*i*-Pr)=	BC=	HC=	B(*i*-Pr)$_2$	
6b	-5.8 [307.4]	145.7 [505.7]	150.9 [462.7]	158.7 (br)	141.1 [31.6]	21.7, 22.3 (br)	51.0

No	δ ^{13}C					δ ^{119}Sn
	EtC(Sn)=	(*i*-Pr)C(Sn)=	EtC(H)=	(*i*-Pr)C(B)=	OMe	
6b	27.1, 15.0 [59.4]	31.4, 23.6 [42.5] [15.3]	21.7, 14.2 [21.7] [8.2]	29.8, 18.1 [80.7] [17.4]	54.5	-81.0

[a] In $CDCl_3$, at 25^{0}C; Coupling constants in Hz: $^nJ(^{119}Sn^{13}C)$ in brackets; (br) denotes broad signals owing to partially relaxed ^{13}C-^{11}B scalar coupling; {br} denotes signals broadened by dynamic processes.

[b] NMR data of **7b**: δ ^{13}C [$^nJ(^{119}Sn,^{13}C)$] = -9.3 {br}, -5.7 {br} (Me_2Sn), 145.0 [452.9] (Sn-C=), 167.2 (br), 25.1 (br), 21.0 (*i*-PrB), 31.0 [71.4], 22.0 [7.0] (*i*-PrC=), 27.6 [46.9], 167.3 16.2 [16.4] (EtC=); δ ^{11}B = 73.5; δ ^{119}Sn = -122.6.

Table 3

^{119}Sn, ^{13}C, ^{11}B NMR data [a] of 2,2,3,7,7,8-hexaethyl-1,4,6,9-tetramethyl-2,7-diborata-1,6-dioxonia-5-stannaspiro[4.4]-nona-3,8-diene (8a) and of the compounds 11 and 11(THF) for comparison

No	$\delta^{13}C$					$\delta\,^{119}Sn$
	SnC(4,9)=	=C(3,8)B	OMe	=CMe	=CEt	
8a[b]	127.8 [626.0]	184.9 (br)	49.5 [n.o.]	18.6 [163.3]	24.9, 12.8 [137.9] [n.o.]	n.o.
8a(ROH)[c]	128.8 [1013.6]	180.3 (br)	48.2 [n.o.]	18.1 [162.4]	24.7, 12.8 [157.5] [18.9]	-296.2
11[d]	128.7 [697.5]	176.3 (br)	49.0 [4.4]	18.7 [146.0]	24.5, 13.8 [116.6] [16.9]	+174.6
11(THF)[e]	127.8 [809.8]	177.3 (br)	47.9 [n.o.]	18.6 [137.9]	25.1, 14.0 [132.4] [18.5]	102.7

[a] In C_6D_6, at 25^{0}C; coupling constants in Hz: $^nJ(^{119}Sn^{13}C)$ in brackets; n.o = not observed; (br) denotes broad signals owing to partially relaxed ^{13}C-^{11}B scalar coupling; {br} denotes broadened signals as a result of dynamic processes..

[b] CD_2Cl_2, 223K; reaction solution. symbol $\delta\,^{13}C$ = 12.2 (br), 10.0, 9.1 (BEt_2). $\delta\,^{11}B$(243K) = 7.2; $h^1/_2(^{11}B\{^1H\}) \approx 800 \pm 50$Hz.

[c] CD_2Cl_2, 223K; reaction solution. $\delta\,^{13}C$ = 13.6 (br), 10.0, 9.9 (BEt_2). $\delta\,^{11}B$(273K) = 5.5; $h^1/_2 \approx 390 \pm 20$Hz.

[d] C_6D_6, 298K; $\delta\,^{13}C$ = 13.4 (br), 10.5 (BEt_2); -1.6[288.3] (Me_2Sn). $\delta\,^{11}B$ = 10.7.

[e] C_6D_6, 298K; $\delta\,^{13}C$ = 13.5 (br), 10.7 (BEt_2); -1.4[376.6] (Me_2Sn). $\delta\,^{11}B$ = 10.7.

2.4. X-Ray structural analysis of $(10a)_2$

The molecular structure of the crystallographically centrosymmetric $\mathbf{(10a)_2}$ is shown in Figure 1 [30], and selected bond lengths and bond angles are given in the legend. There is a central planar four- membered ring accompanied by two almost planar five-membered rings which are in mutual *trans*-positions and in *endo*-positions with respect to the central ring. The five-membered rings form an interplanar angle of 58.8° against the plane of the central ring. The surroundings of the tin atoms are distorted trigonal bipyramidal. The oxygen atom O(2A) of a bridging methoxy group ($d_{Sn(1)\text{-}O(2A)}$ = 205.9 pm), C(1) of the 2,5-dihydro-1,2,5-oxoniastannaboratole fragment and C(11) of the alkenyl group (disordered) lie in the equatorial plane (sum of bond angles 359.8°). The axial positions are occupied each by two oxygen atoms O(1) (oxonia) and the O(2) from the second bridging methoxy group (angle O(1)-Sn(1)-O(2) = 160.3°). This is in agreement with comparable tin oxygen compounds, in which the axial positions are always occupied by oxygen atoms [31–33].

The distance $d_{Sn(1)\text{-}O(2)}$ = 224.6 pm is enlarged with respect to $d_{Sn(1)\text{-}O(2A)}$ (*vide supra*) and indicates a dative O-Sn bond, although it is shorter than for coordinated THF (in **12(THF)**: $d_{Sn\text{-}O(THF)}$ = 242.4 pm [34]).

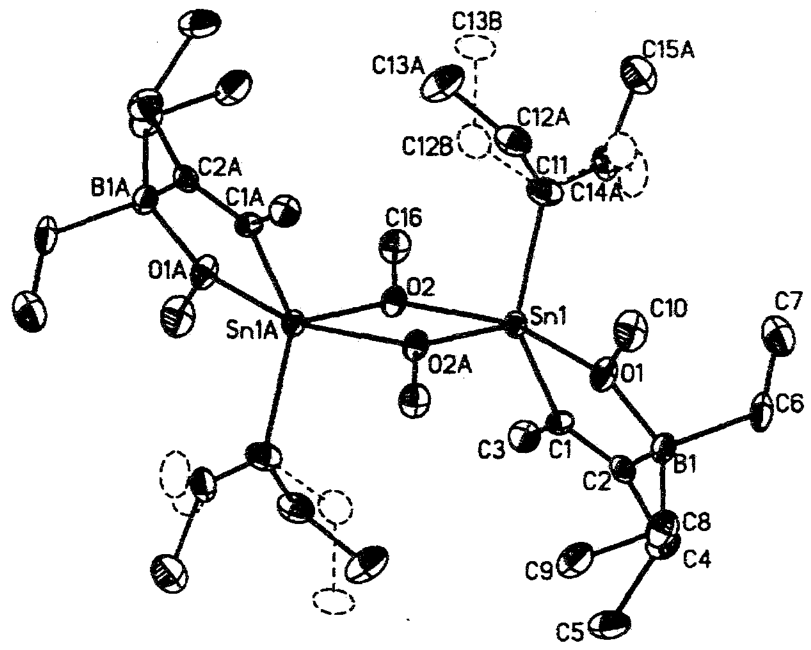


Fig. 1. Molecular structure of the dimer **(10a)$_2$**

Selected bond lengths and angles: Sn(1)-O(2)A 2.059(3), Sn(1)-C(1) 2.096(4), Sn(1)-O(1) 2.129(3), Sn(1)-C(11) 2.131(4), Sn(1)-O(2) 2.246(3), B(1)-O(1) 1.585(5), B(1)-C(8) 1.630(6), B(1)-C(2) 1.631(6), B(1)-C(6) 1.633(6); O(2)A1-Sn(1)-C(1) 119.90(12), O(2)A1-Sn(1)-O(1) 92.13(11), C(1)-Sn(1)-O(1) 83.59(12), O(2)A1-Sn(1)-C(11) 105.67(14), C(1)-Sn(1)-C(11) 134.2(2), O(1)-Sn(1)-C(11) 99.55(14), O(2)A1-Sn(1)-O(2) 70.47(11), C(1)-Sn(1)-O(2) 96.88(12), O(1)-Sn(1)-O(2) 160.30(10), C(11)-Sn(1)-O(2) 94.19(13), O(1)-B(1)-C(8) 109.4(3), O(1)-B(1)-C(2) 103.7(3), C(8)-B(1)-C(2) 114.3(3), O(1)-B(1)-C(6) 109.6(3), C(8)-B(1)-C(6) 109.3(3), C(2)-B(1)-C(6) 110.4(3), C(10)-O(1)-B(1) 118.2(3), C(10)-O(1)-Sn(1) 123.9(3), B(1)-O(1)-Sn(1) 114.9(2), C(16)-O(2)-Sn(1)A1 127.1(2), C(16)-O(2)-Sn(1) 118.1(2), Sn(1)A1-O(2)-Sn(1) 109.53(11).

Table 4

^{119}Sn, ^{13}C, ^{11}B NMR data [a] of the dimer (10a)$_2$

No	δ ^{13}C						δ ^{119}Sn
	SnC(5)=	=C(4)B	SnC(3')=	=C(2')H	MeOB	MeO	
(10a)$_2$[b]	124.1 [970.0]	185.6 (br)	146.3 [756.0]	140.5 [55.0]	50.3 [6.0]	52.6 [13.0]	-235.1 [105.0]

[a] In C_6D_6, at 25^{0}C; coupling constants in Hz: $^nJ(^{119}Sn^{13}C)$ in brackets; (br) denotes broad signals owing to partially relaxed ^{13}C-^{11}B scalar coupling; {br} denotes broadened signals as a result of dynamic processes.

[b] δ $^{11}B(C_6D_6)$= 7.8; $h^1/_2(^{11}B\ \{^1H\}) \approx 400 \pm 20$Hz.
δ $^{13}C(C_6D_6)$= 25.5 [174.0], 15.4 [22.4] (EtC(3')=); 24.4 [81.8], 13.4 [18.5] (EtC(4)=); 18.1 [166.0] (MeC(5)=); 14.5 (MeCH); 15.0(br), 12.9(br), 11.4, 10.5 (BEt$_2$).

^{119}Sn, ^{11}B, ^{13}C NMR data [a] of the 1-alkyl-4,5,5-triethyl-3-methyl-2-[3'-(*E*)-pent-2'-enyl]-(2-propyn-1'-yl)-2,5-dihydro-1,2,5-oxoniastannaboratoles 9a

No	δ ^{13}C						δ ^{119}Sn
	SnC(3)=	=C(4)B	SnC(2')=	=C(2')H	SnC	CMe	
9a[b]	125.4 [792.0]	178.0 (br)	145.8 [606.4]	141.3 [45.0]	83.0 [n.o.]	110.3 [99.8]	-55.8
9a(ROH)[c]	124.3 [978.7]	177.9 [130] (br)	146.3 [755.3]	136.8 [42.5]	85.3 [659.4]	105.3 [131.7]	-190.6
9a(THF)[d]	124.8 [896.3]	180.3 (br)	147.5 [666.9]	139.4 [49.2]	85.3 [n.o.]	107.4 [280.3]	-126.8
9a(EtOH)[e]	125.7	179.4 (br)	147.6	141.5	83.9	110.9	-45.6
9a(*i*-PrOH)[f]	125.0 [795.6]	178.7 (br)	148.0 [592.2]	141.5 [51.2]	84.7 [471.0]	110.7 [108.5]	-60.5

[a] In C_6D_6, at 25°C; coupling constants in Hz: "$J(^{119}Sn^{13}C)$ in brackets; n.o = not observed; {br} denotes broad signals owing to partially relaxed ^{13}C-^{11}B scalar coupling; denotes broadened signals as a result of dynamic processes.

[b] 223K, CD_2Cl_2; reaction solution. 12δ^{13}C = 49.1 (MeO); 24.2 [135.0], 14.8 [22.5] (EtC(2'')=); 24.3 [78.3], 14.5 (EtC(4)=); 18.5 [155.5] (MeC(3)=); 13.1 (MeCH); 12.2, 9.8, 9.8 (BEt_2); 5.1 (MeC≡). δ ^{11}B(243K) = 7.2; $h^1/_2(^{11}B\{^1H\})$ ≈ 800 ± 50Hz.

[c] Coordination to MeOH; 223K, CD_2Cl_2; reaction solution: δ^{13}C = 47.2 (MeO); 24.4 [150.0], 14.4 [25.1] (EtC(2')=); 24.0 [79.6], 13.9 (EtC(4)=); 17.4 [145.0] (MeC(3)=); 13.2 [18.5] (MeCH); 13.5 (br), 10.2, 10.0 (BEt_2); 4.5 (MeC≡); 49.6 (MeOH). δ ^{11}B(263K) = 5.7; $h^1/_2$ ± 20Hz.

[d] Coordination to THF. δ$^{13}C(C_6D_6)$ = 48.8 (MeO); 25.2 [144.9], 14.8 [20.3] (EtC(2')=); 24.9 [96.6], 14.3 [13.0] (EtC(4)=); 18.2 [156.5] (MeC(3)=); 13.6 [19.2] (MeCH); 13.9(br), 0.8, 10.5 (BEt_2); 4.6 (MeC≡); 68.6, 25.6 (THF). δ $^{11}B(C_6D_6)$ = 5.6.

[e] δ$^{13}C(C_6D_6)$ = 60.5, 18.4 (EtO); 25.0, 14.5 (EtC(4)=); 24.7, 14.9 (EtC(2')=); 18.3 (MeC(3)=); 13.7 (MeCH); n.o.; 10.9, 10.7 (BEt_2); 4.8 (MeC≡).

[f] δ$^{13}C(C_6D_6)$ = 70.1 [10.4], 26.1, 25.7 (*i*-PrO); 24.9 [n.o.], 14.4 (EtC(4)=); 24.5 [n.o.], 14.7 [n.o.] (EtC(3')=); 17.8 [n.o.] (MeC(3)=); 13.6 [n.o.] (MeCH); 14.8 (br), 11.1, 11.0 (BEt_2); 4.7 (MeC≡). δ $^{11}B(C_6D_6)$ = 13.2.

3. CONCLUSIONS

It has been shown that the zwitterionic intermediates from 1,1-organoboration reactions possess numerous reactive sites which can be used to form new heterocyclic compounds Interestingly, the methanolysis reaction appears to take place first at the Sn-C= bond, assisted by the presence of the boryl group in cis-position to the stannyl group. This causes novel rearrangements of the boron-bonded alkenyl group.

4.1. General, starting materials and instrumentation

All synthetic work and the handling of compounds was carried out in an argon atmosphere, using carefully dried solvents and dry glass ware, observing all precautions to exclude oxygen and moisture. Starting materials were prepared following literature procedures: **1a,b** [12], **1c** [13], **2** [14]. EI-Mass spectra (70 eV): Varian MAT-CH-7 with a direct inlet. NMR spectra measured from samples in 5 mm tubes: Jeol FX90Q [^{11}B (29.7 MHz), ^{119}Sn (33.6 MHz)]; Bruker AC 300 [^{1}H, ^{11}B (99.0 MHz), ^{13}C (75.5 MHz), ^{119}Sn (111.9 MHz)]; Bruker AM 500 [^{1}H, ^{13}C (125.8 MHz), ^{119}Sn (186.5 MHz)]; chemical shifts are given with respect to the residual signal of the respective deuterated solvent [δ^{1}H(Me$_4$Si) = 0], to the signal of the deuterated solvent [δ ^{13}C(Me$_4$Si) = 0], to external Et$_2$O-BF$_3$ [δ ^{11}B = 0 for $\Xi(^{11}\text{B})$= 32.983971 MHz], and to external Me$_4$Sn [δ ^{119}Sn = 0 for $\Xi(^{119}\text{Sn})$= 37.290665 MHz].

4.2. Syntheses

2,5-Dihydro-3-substituted 4,5,5-trialkyl-2,2-dimethyl-1,2,5-oxoniastannaboratoles 3a–c. A solution of **1** (0.4 mmol) in CHCl$_3$ (0.5 ml) is cooled to -78°C, and MeOH (0.4 mmol; 16.2 µl) is injected. After warming to room temperature and removing of all volatile material *in vacuo* (0.1 Torr) **3a** and **3c** are left in pure state as a colourless liquid or a yellow oil, respectively. The compound **3b** is formed in mixture with **6b**.

3a: ^{1}H-NMR (CDCl$_3$): δ [$^{n}J(^{119}\text{Sn}^{1}\text{H})$] = 0.50 [49.5] (s, 6H, SnMe$_2$); 2.11 (br), 0.50 (br) (10H, BEt$_2$); 1.97 (q), 0.87 (t) (5H, Et); 2.37 (t), 1.29 (m), 0.94 (t) (7H, Pr); 3.23 [9.8] (s, 3H, OMe).

3b:^{1}H-NMR (CDCl$_3$): δ [$^{n}J(^{119}\text{Sn}^{1}\text{H})$] = 0.56 [48.2] (s, 6H, SnMe$_2$); 0.84 (d), (12H, B(CHMe$_2$)$_2$), 2.59 (m), 1.11 (d) (7H, (*i*-Pr)); 2.63 (q), 0.84 (t), (5H, Et); 3.39 [11.7] (s, 3H, OMe); some signals were not assigned due to overlap.

3c:^{1}H-NMR (CDCl$_3$): δ [$^{n}J(^{119}\text{Sn}^{1}\text{H})$] = 0.32 [62.7] (s, 6H, SnMe$_2$); 0.08 (br), 0.43 (t) (10H, BEt$_2$); 1.98 (q), 0.81 (t) (5H, Et); 3.39 [87.0] (s), 2.29 (s) (8H, CH$_2$NMe$_2$); 3.01 [5.5] (s, 3H, OMe).

2,5-Diethyl-1,4-diisopropyl-1-isopropyl(methoxy)boryl-3,3-dimethyl-3-stanna-1,4-pentadien 6b: ^{1}H-NMR (CDCl$_3$): δ [$^{n}J(^{119}\text{Sn}^{1}\text{H})$] = 0.21 [49.9] (s, 6H, SnMe$_2$); 1.06 (d), (12H, B(CHMe$_2$)$_2$), 2.98 (m), 0.97 (d) (7H, (*i*-Pr)C(Sn)=)); 2.42 (q), 0.96 (t), (5H, EtC(Sn)=)); 2.12 (m), 0.98 (m), (5H, EtC(H)=); 2.95 (m), 0.97 (d) (7H, (*i*-Pr)C(B)=); 5.48 (t) (1H, =CH); 3.67 (s, 3H, OMe); some signals were not assigned due to overlap.

Bis{µ-(2-methoxy)-4,5,5-triethyl-2,5-dihydro-1,3-dimethyl-2-[3'-(*E*)-pent-2'-enyl]-1,2,5-oxoniastanna-boratole} (10a)$_2$. A solution of 2 (1.0 g; 2.1 mmol) in hexane (50 ml) is cooled to -78^{0}C, and MeOH (3 ml) is added in one portion. After stirring at room temperature for 48 h all volatile material is removed in vacuo (10^{-3} Torr) a colourless solid is left. Crystallisation from hexane gives 0.4 g (49 %) of **(10a)$_2$** (m.p. 119–122 °C). EI-MS (C$_{32}$H$_{66}$O$_4$B$_2$Sn$_2$ [776]): *m/z* (%)= 357 (38), 189 (100). ^{1}H-NMR (C$_6$D$_6$, 298 K): δ [$^{n}J(^{119}\text{Sn}\ ^{1}\text{H})$] = 5.85 [128.0] (q, 2H;HC(3')=); 3.38 [25.6] [10.2] (s, 6H, OMe); 3.20 [7.1] (s, 6H, MeO-bridge); 2.08 (m. 4H), 0.94 (t, 3H), 0.86 (t, 3H) (Et); 1.90 [110.1] (6H, MeC(3)=); 1.68 [16.0] (d, 6H; MeC(3')=); 0.59 (t, 12H), 0.19 (m, 8H) (BEt$_2$).

4,5,5,-Triethyl-1,3-dimethyl-2-[3'-(*E*)-pent-2'-enyl]-2-(propyn-1'-yl)-2,5-dihydro-1,2,5-oxonia-stannaboratole adducts 9a(EtOH) and (9a(*i*-Pr)OH). The adducts **9a(EtOH)** and **9a(*i*-Pr)OH)** are prepared following the description for **(10a)$_2$** by using EtOH or. (*i*-Pr)OH instead of MeOH. After removing of all readily volatile material *in vacuo*, yellow, viscous liquids are obtained. Attempts of distillation lead to decomposition and crystallisation from various solvents fails.

9a(*i*-Pr)OH): ^{1}H-NMR (C$_6$D$_6$) relevant signals: δ [$^{n}J(^{119}\text{Sn}^{1}\text{H})$] = 6.38 (q, 1H, =CH); 4.33, 1.56, 1.36 (s, d, d, 7H, (*i*-Pr)PrO); 1.88 (s, 3H, MeC(5)=); 1.53 (s, 3H; ≡CMe); 1.10 (d, 3H; MeC(3')=).

4.3. X-Ray structural analysis of the dimer (10a)$_2$

Crystal: C$_{32}$H$_{66}$B$_2$O$_4$Sn$_2$; colourless plate of dimensions 0.32·0.26·0.09 mm, monoclinic, space group P2$_1$/c with lattice parameters a = 1128.3(2), b = 1429.3(3), c = 1176.1(2) pm, β = 100.95(2)°, V = 1862.1(7) ·10^{6} pm^{3}, Z = 2, absorption coefficient μ = 1.372 mm^{-1}, ρ = 1.384 g/cm^{-3}.

Data collection: Siemens P4 diffractometer, Mo-Kα radiation, λ = 71.069 pm (graphite monochromator), 109 K, crystal sealed under nitrogen into glass capillary; 2θ range 3° – 55°, ω-scan type, 4417 reflections collected, 4210 independent (R_{merg} = 0.0298), observed 3871 ($F_0 \geq 4\sigma(F)$), empirical psi-scan absorption correction, min/max transmission factors: 0.90/0.75.

Structure solution and refinement: Patterson Methods, full matrix least squares on F^2 (Siemens-SHELXTL Vers. 5.03, 1994), refinement of 217 parameters, all non-hydrogen atoms with anisotropic temperature factors, the hydrogen atoms were described on calculated positions with the 1.2 (1.5 for methyl groups) fold isotropic temperature factors of the equivalent temperature factors of the corresponding C-atoms applying the riding model; for the disordered C-atoms $C_{(12)}$ to $C_{(15)}$ occupancies were refined and subsequently fixed at 0.6 and 0.4, respectively. The refinement converged at final R indices R^1 = 0.0362 and R^2 (all data) = 0.0968, max./min. residual difference electron density $1.2 \cdot 10^{-6}$ pm^{-3}.

Support of this work by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

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Laboratorium für Anorganische Chemie,
Universität Bayreuth, D-95440 Bayreuth,
Germany
Fax +49(0)921/552157;
e-mail: b.wrack@uni-bayreuth.de

Received May 7, 1999

Institut für Anorganische Chemie,
Universität - GH Essen, Universitätsstr. 5-7,
D-45117 Essen, Germany