

# Isomerisation of Alkenes Bearing Stannyl and Boryl Groups at the C=C Bond

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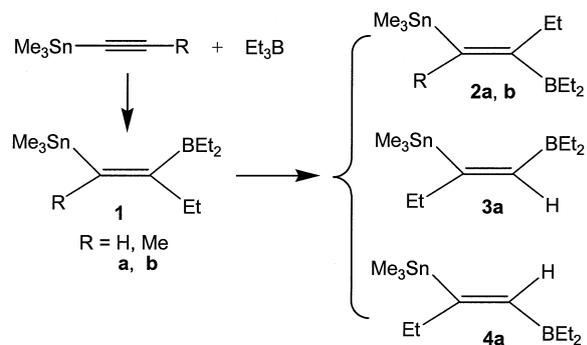
Boron, Tin, Alkenes, Isomerisation, NMR Data

Alkenes bearing organometallic substituents such as boryl and stannyl groups isomerise slowly in the absence of UV irradiation. In addition to *cis/trans* isomerisation the boryl and stannyl group may also exchange places. This is shown for (*Z*)-2-chloro(dimethyl)stannyl-3-diethylboryl-pent-2-ene **5b** (conversion into (*Z*)-3-chloro(dimethyl)stannyl-2-diethylboryl-pent-2-ene **7b**) and 3,4-diethyl-1,1,2,5-tetramethyl-1,2-dihydro-1,3-stannaborole **8b** (conversion into 3,5-diethyl-1,1,2,4-tetramethyl-1,2-dihydro-1,3-stannaborole **9b**). Zwitterionic structures, involving a bridging boryl group with  $\pi$ - $\sigma$  delocalisation, the stabilising effect exerted by a stannyl group in  $\beta$ -position with respect to a positively charged centre, and migration of a stannyl group, are suggested in order to explain the isomerisation. The heterocycle **9b** was prepared independently from the reaction of **7b** with lithium diisopropylamide.

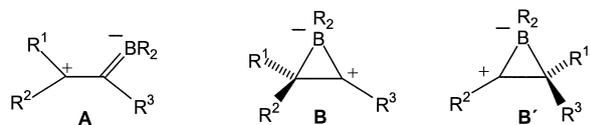
## Introduction

Organometallic substituents can affect the reactivity of alkenes by steric and electronic effects. In this context both boryl [1] and stannyl groups [2] are known to exert a profound influence, and if both groups are linked to the C=C bond, e. g. in *cis*-positions, novel properties may arise. Such organometallic-substituted alkenes are readily available by 1,1-organoboration of alkynyltin compounds [3], and related heterocycles containing one or more C=C bonds are also accessible [3 - 6]. Previously, we have observed that the alkene **1a** isomerises readily at ambient temperature, at day light or in the dark, diluted in hexane solution or as a pure liquid, and particularly fast (few hours) in the presence of THF, into a mixture consisting mainly of the four isomers **1a** - **4a** (Scheme 1) [7]. In contrast, the isomerisation of **1b** into **2b**, under comparable conditions, requires several days, and the isomers **3b** or **4b** were not formed in an appreciable amount [7]. A conclusive explanation of the behaviour of **1a** or **1b** has not been offered at that time.

Canonic structures of alkenylboranes which involve CB(pp) $\pi$  interactions as in **A** are frequently proposed in the literature, although their contribution to the ground state of the molecule may be small, especially if steric conditions prevent a favourable coplanar arrangement of the boryl group with respect to the C=C plane [8]. Another zwitterionic structure **B**, in which  $\pi$ - $\sigma$  delocalisation is involved [9, 10], has received much less attention. However, structures of type **B** may become more important if for example  $R^1$  is a stannyl group as in the case of **1**. Considering the migratory aptitude of a stannyl group (see **B'**) together with its stabilizing effect of a positive charge in  $\beta$ -position [10], **B** (*cis/trans* isomerisation from **1** into **2** which could also be traced to **A**) and **B'** (isomerisation of **1a** into **3a** and **4a**) can account for the isomers shown in Scheme 1. Two further examples of isomerisation,



Scheme 1.

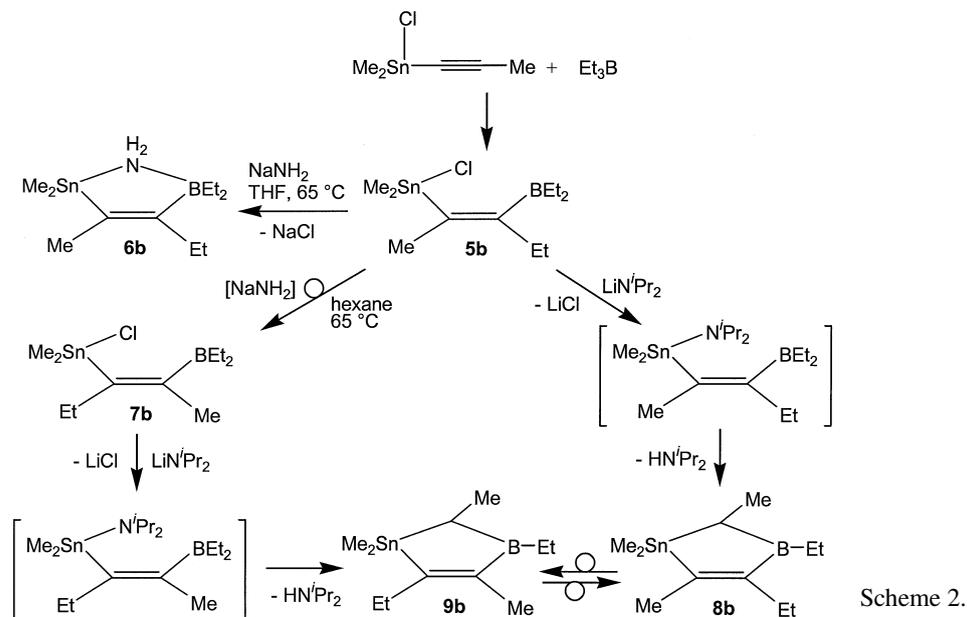


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Table 1.  $^{11}\text{B}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data <sup>[a]</sup> of the alkenes **5b** and **7b**.

	$\delta^{13}\text{C}$ (SnC=)	$\delta^{13}\text{C}$ (BC=)	$\delta^{13}\text{C}$ (SnMe <sub>2</sub> )	$\delta^{13}\text{C}$ (BEt <sub>2</sub> )	$\delta^{13}\text{C}$ (Me)	$\delta^{13}\text{C}$ (Et)	$\delta^{11}\text{B}$	$\delta^{119}\text{Sn}$
<b>5b</b>	134.3 [611.0]	166.7 (br) [85]	-1.0 [345.0]	21.7 (br), 8.7	18.8 [83.6]	23.3 [108.8], 13.1 [11.9]	+82.3	+81.1
<b>7b</b>	141.8 [607.8]	158.7 (br) [90]	-0.1 [340.8]	20.6 (br), 9.2	15.0 [124.6]	26.2 [87.7], 15.1 [10.9]	+80.1	+92.7

<sup>[a]</sup> Coupling constants  $J(^{119}\text{Sn}, ^{13}\text{C})$  ( $\pm 0.5$  Hz) are given in brackets; (br) denotes  $^{13}\text{C}$  NMR signals broadened by one-bond  $^{13}\text{C}$ - $^{11}\text{B}$  partially relaxed scalar coupling.



one for a non-cyclic alkene, and the other one for a cyclic alkene are presented in this work.

## Results and Discussion

### Rearrangement of (Z)-2-chloro(dimethyl)stannyl-3-diethylboryl-pent-2-ene **5b**

In the alkene derivative **5b**, comparable with **1b**, the tin atom bears a chloro function, and therefore **5b** has already been used as a versatile reagent in further transformations [11 - 14]. In contrast to **1b**, **5b** can be kept at room temperature or in a refrigerator for years without significant isomerisation. Scheme 2 summarises results mainly obtained in this study.

In the case of the reaction of **5b**, dissolved in THF, with commercially available powdered  $\text{NaNH}_2$  at 65 °C,  $\text{NaCl}$  is eliminated to give the expected product **6b** [11, 15]. If the same reaction is carried out in boiling hexane, it appears at a first glance that **5b** does not react. However, NMR spectra (Table 1)

show quantitative rearrangement of **5b** into **7b**, in which the stannyl and boryl groups have exchanged places. It is tempting to assume that intermediate structures of type **B**, and in particular **B'**, are responsible for the isomerisation which is apparently induced by physical interactions of **5b** with the surface of solid  $\text{NaNH}_2$ . The process itself corresponds to the isomerisation of **1a** into **3a**. The absence of *cis/trans*-isomerisation in the cases of **5b** and **7b** can be explained by the presence of weak Sn-Cl-B bridges (see [16] for Si-Cl-B or [17] for Ti-Cl-B bridges).

### Rearrangement of 3-ethyl-1,2-dihydro-1,1,2,5-tetramethyl-1,3-stannaborole **8b**

The reaction of **5b** with lithium diisopropylamide (LDA) proceeds by elimination of  $\text{LiCl}$  (Scheme 2). In contrast with the  $\text{NH}_2$  group in **6b**, the  $\text{N}^i\text{Pr}_2$  group is too bulky for strong coordinative N-B bonding [14b]; instead, the  $\text{N}^i\text{Pr}_2$  group abstracts a proton from one of the B-Et groups and is elimi-

Table 2.  $^{11}\text{B}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data <sup>[a]</sup> of the 1,3-stannaborole derivatives **8b** and **9b**.

	$\delta^{13}\text{C}(5)$ (SnC=)	$\delta^{13}\text{C}(4)$ (BC=)	$\delta^{13}\text{C}(2)$ (2-Me)	$\delta^{13}\text{C}$ (SnMe <sub>2</sub> )	$\delta^{13}\text{C}$ (BEt)	$\delta^{13}\text{C}$ (Me)	$\delta^{13}\text{C}$ (Et)	$\delta^{11}\text{B}$	$\delta^{119}\text{Sn}$
<b>8b</b>	158.9 [453.3]	168.5 (br) [73.9] <sup>[b]</sup>	29.5 (br) [143.4], 15.1 [11.9]	-8.1 [274.7], -10.2 [301.4]	13.7 (br), 8.6	19.8 [61.0] 23.3 [83.9]	+75.2 +7.4		
<b>9b</b> <sup>[b]</sup>	169.4 [445.6]	159.3 (br) [81.5]	27.7 (br) [145.3], 16.5 [12.0]	-5.8 [274.2], -9.3 [304.0]	15.2 (br), 8.1	16.3 [94.0]	26.6 [52.5], 75.0	+7.5	

<sup>[a]</sup> Coupling constants  $J(^{119}\text{Sn}, ^{13}\text{C})$  ( $\pm 0.5$  Hz) are given in brackets; (br) denotes  $^{13}\text{C}$  NMR signals broadened by one-bond  $^{13}\text{C}$ - $^{11}\text{B}$  partially relaxed scalar coupling; <sup>[b]</sup> at  $-40$  °C in  $\text{CDCl}_3$ .

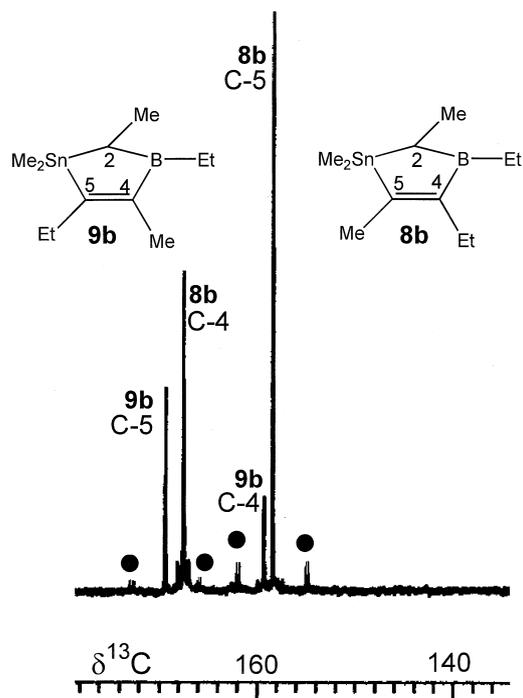


Fig. 1. 62.9 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (in  $\text{CDCl}_3$  at 233 K) of the final mixture containing **8b** and **9b** in the ratio 76:24, showing the range of the olefinic carbon atoms.  $^{117/119}\text{Sn}$  satellites corresponding to  $^1J(\text{Sn}, ^{13}\text{C})$  are marked by filled circles. The  $^{13}\text{C}$  NMR signals of the carbon atoms linked to boron are sharpened by low-temperature  $^{11}\text{B}$  quadrupolar decoupling, and  $^{117/119}\text{Sn}$  satellites corresponding to  $^2J(\text{Sn}, ^{13}\text{C})$  can be observed.

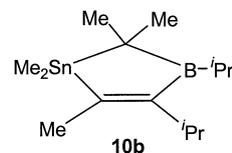
nated as  $\text{HN}^i\text{Pr}_2$  to leave the heterocycle **8b** [14a]. Keeping pure samples of liquid **8b** in sealed ampoules or  $\text{C}_6\text{D}_6$  solutions of **8b** in sealed NMR tubes for several months at ambient temperature leads to mixtures containing **8b** and a small amount ( $< 5\%$ ) of **9b**, and finally after six years, when no further changes take place, a 76:24 mixture of **8b** and **9b** is obtained (Fig. 1, Table 2). Pure samples of **9b** are

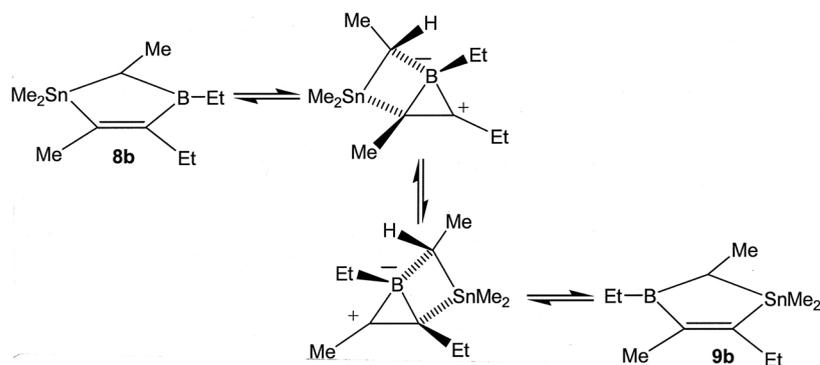
obtained independently, in analogy to the synthesis of **8b**, by the reaction of **7b** with LDA (Scheme 2). The pure compound **9b** also isomerises slowly to give a mixture of **8b** and **9b**.

In both compounds, **8b** and **9b**, the magnitude of the coupling constants  $^1J(^{119}\text{Sn}, ^{13}\text{C}(2))$  is fairly small as a result of the linkage of C(2) to the electropositive boron atom. At room temperature the  $^{117/119}\text{Sn}$  satellites are not observed at all owing to the severely broadened (partially relaxed [18] scalar  $^{13}\text{C}$ - $^{11}\text{B}$  coupling) central  $^{13}\text{C}(2)$  NMR signal. However, at  $-40$  °C quadrupolar decoupling [18, 19] of the  $^{11}\text{B}$  nucleus gives rise to sharper  $^{13}\text{C}(2)$  NMR signals (see also Fig. 1 for the range of the olefinic carbon atoms), and a 2D  $^{13}\text{C}/^1\text{H}$  HETCOR experiment allows for the comparison of the signs of  $^2J(^{119}\text{Sn}, ^1\text{H}(2))$  (known to be  $> 0$  [20]) and  $^1J(^{119}\text{Sn}, ^{13}\text{C}(2))$  which, according to the negative tilt [21] of the relevant cross peaks are opposite. Therefore, the coupling constants  $^1J(^{119}\text{Sn}, ^{13}\text{C}(2))$  are negative as is true for most values  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  [20] (since  $\gamma(^{117/119}\text{Sn}) < 0$ , reduced coupling constants  $^1K(^{117/119}\text{Sn}, ^{13}\text{C}) > 0$ ).

Since the interconversion of **8b** and **9b** takes place at comparable rates in the pure liquid and in solution, an intramolecular mechanism must be assumed. As shown in Scheme 3, structures with  $\pi$ - $\sigma$  delocalisation and migration of the stannyl group can account for the isomerisation.

Kinetic hindrance plays an important role, considering the slow process of isomerisation of **1b** and **8b** when compared with **1a**. Prolonged heating of pure samples or solutions of **8b** at  $80$  °C induces mainly slow decomposition into undefined prod-



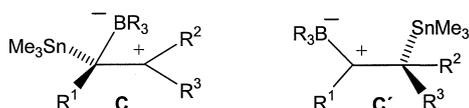


Scheme 3.

ucts. In this context it is noteworthy that **10b** [14a] does not isomerise at room temperature.

### Conclusions

Isomerisation of alkenes bearing organometallic substituents such as boryl and stannyl groups takes place much more readily than with other alkenes, and it does not require UV irradiation. Zwitterionic structures such as **B** arising from  $\pi$ - $\sigma$  delocalisation are proposed as potential candidates for explaining the isomerisation. Although there are numerous examples of three-membered rings containing a boron and two carbon atoms [10f,22], the structures **B** are not likely to present intermediates which can be isolated. However, such structures may have a more general bearing, since they can also be considered in the reaction of alkenyltin compounds with triorganoboranes (see **C**). These reactions still await experimental verification, and they are an attractive challenge in organotin and boron chemistry.



### Experimental Section

The alkene **5b** and the heterocycle **8b** were prepared as described [14,23]. Sodium amide was filtered off from a commercially available oil suspension, washed with hexane several times, and dried *in vacuo*. LDA was freshly prepared from diisopropyl amine and butyl lithium (1.6 M in hexane). NMR spectra were recorded at 23 °C on Bruker DRX 500, AC 300 or ARX 250 spectrometers, each equipped with a multinuclear unit, using  $C_6D_6$  solutions in sealed 5 mm tubes (*ca.* 40 mg of the compound in 0.6 ml solvent) if not mentioned otherwise. Chemical shifts are given with respect to  $Me_4Si$

[ $\delta^1H(C_6D_6)$  = 7.15;  $\delta^{13}C(C_6D_6)$  = 128.0;  $\delta^{13}C(CDCl_3)$  = 77.0],  $\delta^{11}B(BF_3-OEt_2)$  = 0 for  $\Xi(^{11}B)$  = 32.083971 MHz, and  $\delta^{119}Sn(Me_4Sn)$  = 0 for  $\Xi(^{119}Sn)$  = 37.290665 MHz. The  $\pi/2$  pulse angles for  $^1H$ ,  $^{13}C$  and  $^{119}Sn$  frequency channels were carefully calibrated. INEPT [24] experiments for  $^{119}Sn$  NMR were based on  $^{2,3J}(^{119}Sn, ^1H) \approx 50$  - 90 Hz.

#### (Z)-3-Chloro(dimethyl)stannyl-2-diethylboryl-pent-2-ene **7b**

A solution of **5b** (1.62 g, 5 mmol) in hexane (15 ml) is kept stirring at -78 °C, and powdered  $NaNH_2$  (0.30 g, 7.7 mmol) is added in one portion. After warming to room temperature the mixture is heated at 65 °C for 3 h. Then, insoluble material is filtered off, the solvent removed in a vacuum, and the colourless residue is distilled at reduced pressure to give **7b** as a colourless liquid (b. p. 78 - 82 °C/0.1 mbar; 1.26 g; 78%). EI MS spectra (70 eV) are not useful to distinguish between **5b** and **7b**.  $^1H$  NMR (500.13 MHz;  $C_6D_6$ ):  $\delta$  [ $J(^{119}Sn, ^1H)$ ] = 0.41 [53.8] (s, 6 H,  $Sn(CH_3)_2$ ), 2.30 [88.8] (q, 2 H,  $=CCH_2$ ), 1.49 [14.0] (s, 3 H,  $=CCH_3$ ), 0.90 - 1.20 (m, 13 H,  $B(CH_2CH_3)_2$ ,  $=CCH_2CH_3$ ).

#### 3,5-Diethyl-1,1,2,4-tetramethyl-1,2-dihydro-1,3-stannaborole **9b**

The alkene **7b** (1.17 g, 3.77 mmol), dissolved in hexane (5 ml), is added under vigorous stirring in one portion to a suspension of LDA (0.31 g, 3.77 mmol) in toluene (15 ml) cooled at -78 °C. After warming to room temperature the mixture is heated to reflux for 5 min., and then insoluble material is filtered off, all readily volatile materials are removed in a vacuum, and the residue is distilled under reduced pressure. The product **9b** is obtained as a colourless liquid (b. p. 69 - 72 °C/0.01 mbar; 0.98 g; 93%).  $^1H$  NMR (250.13 MHz;  $C_6D_6$ ):  $\delta$  [ $J(^{119}Sn, ^1H)$ ] = 0.14 [53.4] (s, 3 H,  $SnCH_3$ ), 0.37 [52.9] (s, 3 H,  $SnCH_3$ ), 0.95 (d, 3 H, 2- $CH_3$ ), 1.55 (q, 1 H, 2-H), 1.83 [13.9] (s, 3 H,  $=CCH_3$ ), 2.30, 2.10, 1.00 (m, m, t, 5 H,  $=CCH_2CH_3$ ), 1.10 - 0.90 (m, 5 H,  $BCH_2CH_3$ ).

*Acknowledgements*

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