Competition between Intra- and Inter-molecular Reactions of Borates: a New Route to 1,4-Dihydro-1,4-distannines

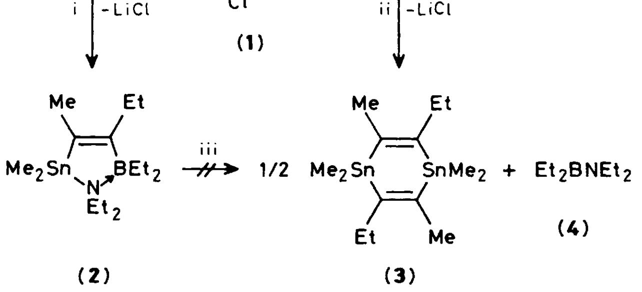
Susanna Kerschl and Bernd Wrackmeyer*

Laboratorium für Anorganische Chemie, Universität Bayreuth, Universitätsstr. 30, D-8580 Bayreuth, Federal Republic of Germany

The reaction of the system (*E*)-2-dimethyl(chloro)stannyl-3-diethylborylpent-2-ene (**1**)–$LiNEt_2$ in hexane can be controlled to give 1,4-dihydro-1,1,2,4,4,5-hexamethyl-3,6-diethyl-1,4-distannine (**3**) in high yield, demonstrating the intermediacy of aminoborate (**5**) and the preference (under the reaction conditions) of intermolecular electrophilic attack at the B–C= bond accompanied by final elimination of LiCl and Et_2NBEt_2 (**4**).

Organoboration of alkynylstannanes[1] provides a convenient stereoselective route to useful alkene derivatives. Functionally substituted tin compounds like (**1**) (Scheme 1) are of particular interest with regard to various intramolecular reactions. Compound (**1**) has already served as a starting material in the synthesis of 1,2-dihydro-1,3-stannaboroles.[2] Nucleophiles will attack (**1**) either at the tin or at the trigonal boron atom. The course of the reaction may be controlled by selecting the reaction conditions and/or by the nature of the nucleophile. The intermediacy of borates in such reactions has been shown for the first time for the reaction between (**1**) and *N*-lithio-azoles.[3] This communication describes the behaviour of the system (**1**)–$LiNEt_2$ in hexane.

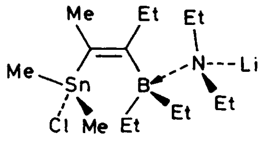
If the first step in the reaction between $LiNEt_2$ and (**1**) involves the formation of an aminoborate (**5**) the most likely product from an intramolecular borate reaction would be compound (**2**) which has already been reported.[2,4] However, bearing in mind the bridging role of the NEt_2 unit in (**5**) in the absence of other donor groups, the borate molecules (**5**) will be present as associated species in hexane solution. Therefore, intermolecular reactions are also conceivable. In contrast to the intramolecular reaction electrophilic attack (accompanied by LiCl elimination) may then take place at one of the B–C bonds instead of at the B–N bond.



Scheme 1. *Reagents and conditions:* i, $LiNEt_2$, hexane, −78 °C → ambient temp., reflux, 5 min; ii, $LiNEt_2$, hexane, −78 °C, work-up; iii, heating to *ca.* 150 °C did not afford (**3**) (or isomer) from (**2**); decomposition products [not including (**4**)] were obtained.

We noted the formation of different products depending on the amount and polarity of the solvent used for the system (**1**)–$LiNEt_2$. In a systematic study all experimental conditions were kept constant except for the amount of solvent (hexane), and it was found that on dilution of the reaction mixtures compound (**2**) was formed exclusively. In concentrated solutions only a small amount of (**2**) (<2%) and a high yield of the 1,4-dihydro-1,4-distannine (**3**) together with diethylaminodiethylborane (**4**) was obtained (Scheme 1). We assume that the small amount of non-polar solvent helps to maintain aggregation of the borate molecules. This favours the intermolecular reaction while the intramolecular reaction is slow on steric grounds. Furthermore, the aminoborane (**4**) may be regarded as a good leaving group.

In a typical reaction 10 mmol of (**1**) in 5 ml of hexane are added (at −78 °C) to a freshly prepared suspension of 10 mmol $LiNEt_2$ in less than 20 ml of hexane. The mixture is allowed to reach ambient temperature within 0.5 h and it is then heated to reflux for 5 min. The ^{11}B n.m.r. spectrum of the reaction solution shows a weak signal for (**2**) [δ (^{11}B) +1.6 p.p.m.[4]] and a strong signal for the aminoborane (**4**) [δ (^{11}B) +46.0 p.p.m.[5]]. Filtration and removal of all volatile material, including (**4**) leaves compound (**3**) as a colourless, oily liquid containing less than 2% of (**2**). Distillation gave 1.84 g (85%) of pure (**3**) (b.p. 94—96 °C/1.33 Pa).



(5)

The structure of (**3**) is proved convincingly by mass and ^{1}H, ^{13}C, and ^{119}Sn n.m.r. spectroscopy.† The double set of $^{117/119}$Sn satellites of relevant ^{1}H or ^{13}C resonances shows the presence of two tin atoms in the molecule. The ^{119}Sn resonance of (**3**) is found in a typical range[6,7] and the observation of the large coupling constant [^3J(^{119}Sn^{117}Sn)][6] corroborates the proposed structure. Very weak signals in the ^{1}H, ^{13}C n.m.r. spectra and two weak ^{119}Sn resonances (1:1) (<3%) indicate the presence of an isomer of (**3**). The selective formation of (**3**) is also in accord with an intermolecular reaction. An intramolecular reaction should give a more statistical mixture of isomers. Thus far, only one similar compound, the 1,4-dihydro-1,1,4,4-tetramethyl-1,4-distannine,[8] has been prepared *via* hydrostannation, followed by a laboured work-up procedure. The method reported here leads for the first time to peralkylated 1,4-dihydro-1,4-distannines and it can be carried out on a large scale. Clearly, 1,4-dihydro-1,4-distannines are attractive reagents in organometallic synthesis.[9]

The observation of the electrophilic attack at the B–C= bond in aminoborates similar to (**5**), followed by lithium halide and aminoborane elimination, is of interest generally and important in the chemistry of organoborates.[10] Initial results for the reaction of the system (*E*)-2-trimethylstannyl-3-diethylborylpent-2-ene–LiNEt$_2$ in hexane with Me$_3$SnCl indicate that *cis*-bis(trimethylstannyl)alkenes can be prepared. A full account of this together with the results for other halides will be given elsewhere.[11]

The present report shows that the reactivity of aminoborates may be controlled by selecting the reaction conditions. In this context the competition between intra- and intermolecular reactions is particularly intriguing.

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

Received, 7th February 1986; Com. 175

---

† *m/z* (20 eV): M^+ 436 (*ca.* 1%); 218 (M^+ − 218, 100%). N.m.r. [Bruker WP 200, 27—28 °C, *ca.* 15% in C$_6$D$_6$, δ values in p.p.m. with respect to internal Me$_4$Si (^{1}H, ^{13}C) and external Me$_4$Sn (^{119}Sn) and coupling constants J(^{119}Sn^{1}H), J(^{119}Sn^{13}C) in Hz given in square brackets]: δ(^{1}H): 0.13 {s, 12H [51.3] SnMe}; 1.91 {s, 6H [49.5, 12.5] =CMe}; 2.36 {q, 4H [63.1, 8.0]}; 0.92 {t, 6H, =CEt}; there is no change in the ^{1}H n.m.r. spectra at low temperature (−80 °C, in CD$_2$Cl$_2$) which indicates that ring inversion is very fast on the n.m.r. time scale. δ(^{13}C): −8.5 {[308.2, 7.3] SnMe}; 19.5 {[75.7, 64.6] =C*Me*}; 27.1 [69.0, 61.6]; 14.7 {[11.0, 11.0] =C*Et*}; 153.2 {[524.9, 52.5] =*C*Me}; 161.8 {[531.0, 42.7] =*C*Et}; δ(^{119}Sn): −154.6, ^3J(^{119}Sn^{117}Sn) 1477 Hz.

References

1 B. Wrackmeyer, *Rev. Silicon, Germanium, Tin, Lead Compd.*, 1982, **6**, 75.

2 S. Kerschl and B. Wrackmeyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1199.

3 S. Kerschl and B. Wrackmeyer, *J. Chem. Soc., Chem. Commun.*, 1986, 403; S. Kerschl and B. Wrackmeyer, *Z. Naturforsch., Teil B*, 1986, **41**, in the press.

4 S. Kerschl and B. Wrackmeyer, *Z. Naturforsch., Teil B*, 1985, **40**, 845.

5 H. Nöth and B. Wrackmeyer, 'NMR of Boron Compounds,' in 'NMR-Basic Principles and Progress,' vol. 14, ed. P. Diehl, E. Fluck, and R. Kosfeld, Springer, Berlin, 1978.

6 H.-O. Berger, H. Nöth, and B. Wrackmeyer, *Chem. Ber.*, 1979, **112**, 2866.

7 B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.*, 1985, **16**, 73.

8 G. E. Herberich and B. Hessner, *Z. Naturforsch., Teil B*, 1978, **33**, 180.

9 G. E. Herberich and B. Hessner, *Chem. Ber.*, 1982, **115**, 3115.

10 R. Köster, *Pure Appl. Chem.*, 1977, **49**, 765; A. Suzuki, *Acc. Chem. Res.*, 1982, **15**, 178; A. Pelter, *Chem. Soc. Rev.*, 1982, **21**, 191.

11 B. Wrackmeyer, manuscript in preparation.