Journal of Organometallic Chemistry, 321 (1987) 25–32
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOBORATION OF ALKYNYLSTANNANES

XIX *. STANNACYCLOPENTADIENES VIA ORGANOBORATION OF DIETHYNYLDIMETHYLSTANNANE WITH *B*-ALKYL-9-BORABICYCLO[3.3.1]NONANES

CHRISTOPH BIHLMAYER, SULTAN T. ABU-ORABI and BERND WRACKMEYER*

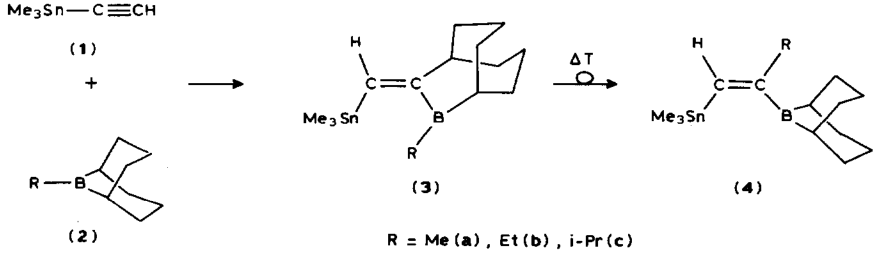
Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 10 12 51,
D - 8580 Bayreuth (F.R.G.)

(Received September 30th, 1986)

Summary

Tricyclic heterocycles (**8**) containing a stannacyclopentadiene unit are obtained as the major products ($>$ 80%) from the reaction between diethynyldimethylstannane and *B*-alykyl-9-borabicyclo[3.3.1]nonanes (**2**). By comparison with the analogous reaction of ethynyltrimethylstannane (**1**) it is shown that compounds **8** are the kinetically controlled products. Assignments of the structure of **8** and those of some minor products are based on multinuclear NMR spectra (^{1}H, ^{11}B, ^{13}C, ^{119}Sn NMR).

Stannacyclopentadienes are attractive reagents for the synthesis of other metallacyclopentadienes [2,3]. We have shown that the reaction between various bis(alkynyl)stannanes and trialkylboranes, R_3B provides a convenient route to stannacyclopentadienes [4,5]. So far, only noncyclic trialkylboranes (R = Me, Et, i-Pr) have been used for the organoboration of bis(alkynyl)stannanes. Initial results for the reaction of cyclic organoboranes with monoalkynylstannanes showed that in the case of boracyclopentanes the enlargement of the five-membered ring is the preferred reaction [6], whereas in the case of *B*-alkyl-9-borabicyclo[3.3.1]nonanes (**2**), it was possible to distinguish (eq. 1) between the kinetically controlled product (**3**) and the thermodynamically controlled product (**4**) (R = Et [7]).



(1)

---

* For part XVIII, see ref. 1.

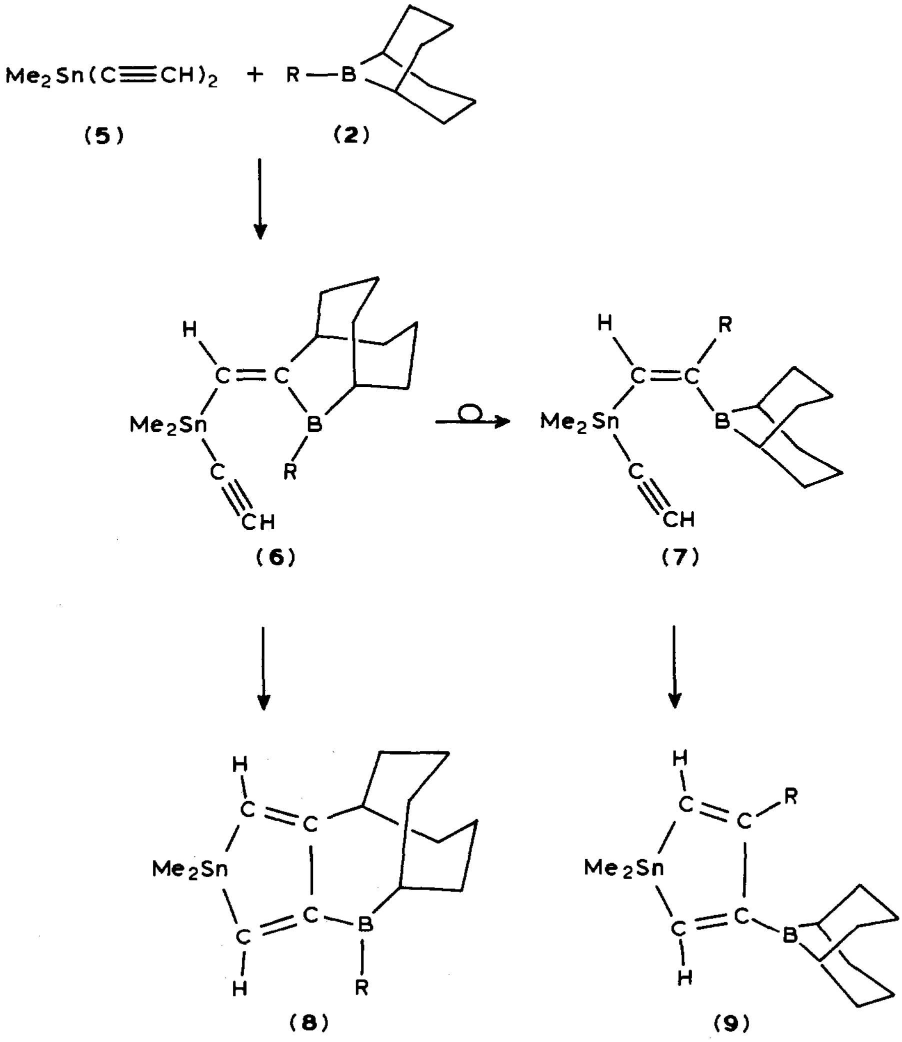
0022-328X/87/$03.50

We report here on the reaction between diethynyldimethylstannane (**5**) and *B*-alkyl-9-borabicyclo[3.3.1]nonanes (R-9-BBN; R = Me (**2a**), Et (**2b**), i-Pr (**2c**)).

Results and discussion

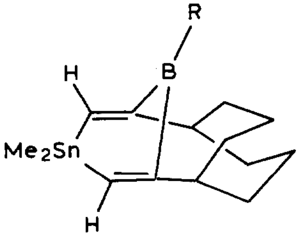
The formation of stannacyclopentadienes via organoboration may be regarded as a two-step process [5,8] in which the first step (Scheme 1) corresponds to the reaction shown in eq. 1. The structure of the stannacyclopentadiene (**8** or **9**) finally formed thus depends on whether kinetically (**6**) or thermodynamically controlled product (**7**) is formed in the first step.

Mixing of **5** and **2** at −78°C in hexane or THF and warming to room temperature gave a yellowish reaction solution. The ^{11}B, ^{119}Sn NMR spectra showed

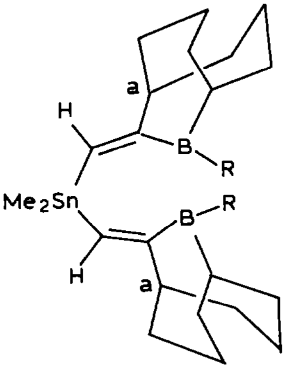


SCHEME 1

that compounds **5** and **2** react in a 1/1 ratio. After removal of the solvent, the ^{1}H and ^{13}C NMR spectra showed that more than 80% of **8** was formed in all cases. A small amount of **9c** was identified. Weak NMR signals were found for other products, in addition to **9a** or **9b**, formed along with **8a,b**; the $\delta(^{119}Sn)$ data indicate that they are 1-stanna-4-bora-2,5-cyclohexadienes, with the structure **10**, and a noncyclic bis(alkenyl)stannane, **11**. The formation of the latter compound may be due to the use of a small excess of **2** in the reaction.



(10)



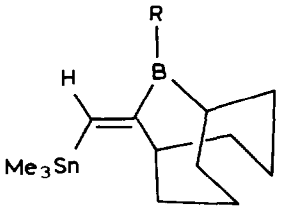
(11)

	10a	**10b**
	R = Me	R = Et
$\delta(^{119}Sn)$	−119.0	−120.4

	11a	**11b**
	R = Me	R = Et
$\delta(^{119}Sn)$	−85.5	−94.8
$\delta(^{13}C)$	148.6 (SnC=)	
$(J(^{119}Sn^{13}C))$	(405.3)	
	168.7 (BC=)	
	49.9 (C(a))	
	(68.4)	

Both types of compounds were previously obtained as the major products from organoboration reactions of other bis(alkynyl)stannanes and their ^{119}Sn shifts were recorded [8,9]. There is a considerable amount of **11a** present (~ 15—20%), and its ^{13}C NMR signals readily reveal its identity. Attempts to purify **8** by distillation led to complete decomposition. In the case of **8b**, heating in benzene at 80 °C for 10 h also induced decomposition. It is conceivable that dehydroboration [10] followed by various irreversible reactions precedes the reversible deorganoboration [11,12]. Because of thermal decomposition the thermodynamically favoured isomers cannot be obtained. Attempts to crystallize compounds **8** at low temperature from pentane solutions were unsuccessful. The reaction of **8** with methanol or acetic acid did not give identified products. At present, the characterization of **8** is mainly based on NMR spectra.

We also carried out the corresponding reaction between ethynyltrimethylstannane, **1**, and **2** (eq. 1) under the conditions used for the reactions in Scheme 1, and after warming to room temperature (**3a**) was formed selectively (> 95%), whereas **3b** is accompanied by ca. 50% **4b** [7], and **3c** by its *Z*-isomer **12c** (ca. 30%).



(12) (R = i-Pr)

Previous work [7] has shown that **3b** isomerizes to the *Z*-isomer **12b** upon prolonged heating in THF. Apparently this process is much faster in the case of **3c**. In contrast to **3b** and **3c**, compound **3a** can be distilled without decomposition or rearrangement.

The selective formation of **3a** is consistent with the absence of **9a** after the reaction between **5** and **2a**. The absence of **9b** suggests that the formation of **8b** (Scheme 1) is fast compared to the rearrangement to the thermodynamically controlled product **7b**. Interestingly, **9c** is found as a minor product, although **4c** could not be observed in the reaction of the type shown in eq. 1. This indicates that the formation of **8c** is much slower than that of **8b**, permitting partial rearrangement into **7c**, followed by formation of **9c**.

NMR spectra

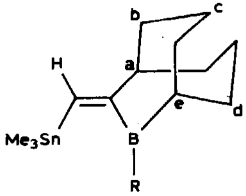
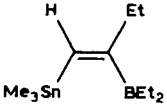
The ^{13}C, ^{11}B and ^{119}Sn NMR data for the compounds **3a,b,c** and **8a,b,c** are given in Tables 1 and 2, respectively. The ^{11}B resonances are all very broad ($h_{1/2} > 400$ Hz) owing to the efficient ^{11}B-quadrupolar relaxation and so in mixtures of **3c**, **12c**, and **8c/9c**, **8a** and **10a/11a**, or **8b** and **10b**, **11b**, the ^{11}B resonances of the components are not resolved. The ^{119}Sn resonances of the components are readily resolved, except for those for **8c/9c**, which are probably very similar. Both $\delta(^{11}\mathrm{B})$ [13] and $\delta(^{119}\mathrm{Sn})$ values [8,14] fall in the expected range. The $\delta(^{119}\mathrm{Sn})$ data are particularly helpful in distinguishing between the structures of the five-membered ring **8**, the six-membered ring **10**, and the noncyclic compound **11** [8]. The relative linewidths of the ^{119}Sn resonances enable assignment of the structures of the *E*-, *Z*-isomers **3c/12c**. The broader ^{119}Sn resonance for **12c** results from $|^3J(^{119}\mathrm{Sn}^{11}\mathrm{B})_{trans}| > |^3J(^{119}\mathrm{Sn}^{11}\mathrm{B})_{cis}|$ [15], confirming the structural assignment based on the ^{13}C NMR data.

The ^{13}C NMR spectra provide conclusive information on the structure of compounds **8**. They show the characteristic pattern of the olefinic ^{13}C resonances of the stannacyclopentadiene unit with three sharp ^{13}C resonances (accompanied by typical $^{117/119}$Sn satellites for $^1J(\mathrm{Sn}^{13}\mathrm{C})$ and $^{2/3}J(\mathrm{Sn}^{13}\mathrm{C})$ and one broad ^{13}C resonance of the boron-bonded carbon atom [4,5]. The assignment of the ^{13}C(2,5) resonances is based on a two dimensional ^{1}H/^{13}C shift correlation [16], and the ^{1}H(5) resonance is readily assigned by an appropriate NOE difference experiment [17] (irradiation of the CH(a) resonance and observation of the ^{1}H(5) resonance). The enlargement of the 9-BBN ring by a C–C unit is further confirmed by (i) the presence of the ^{13}C resonances for the BR group, (ii) the presence of the ^{13}C(a) resonance of a tertiary carbon atom with $^{117/119}$Sn satellites typical for $^3J(\mathrm{Sn}^{13}\mathrm{C})$ coupling across a C=C double bond [14b], and (iii) the different ^{13}C(b,d) resonances. The ^{13}C NMR data are similar to those obtained for other stannacyclopen-

(*Continued on p. 31*)

TABLE 1

^{11}B, ^{119}Sn AND ^{13}C NMR DATA[a] FOR ORGANOBORATION PRODUCTS OF ETHYNYLTRIMETHYLSTANNANE

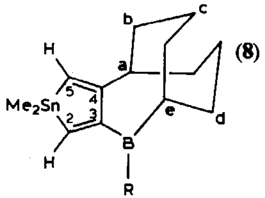
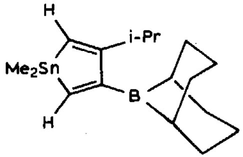
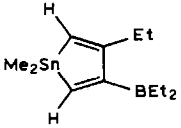
	$\delta(^{119}Sn)$	$\delta(^{11}B)$	$\delta(^{13}C)$								
			SnC=	BC=	SnMe	BR	C(a)	C(b)[b]	C(c)	C(d)[b]	C(e)
 (3)											
3a, R = Me	−61.0	79.2	146.6 (479.0)	174.0 (br)	−6.8 (345.5)	14.2 (br)	51.2 (85.0)	33.6	23.3	28.8	33.9 (br)
3b, R = Et	−60.4	83.0	142.9 (482.0)	174.0 (br)	−6.9 (344.2)	21.1, 9.5 (br)	50.6 (86.7)	33.3	22.9	28.5	29.8 (br)
3c, R = i-Pr	−60.7	81.0	144.9 (479.5)	172.5 (br)	−6.9 (345.0)	24.5, 19.9 (br)	51.1 (86.6)	33.6	22.6	28.8	31.5 (br)
	−55.1	83.5	124.6 (503.0)	173.0 (br)	−8.7 (336.5)	21.4, 8.5 (br)	32.3 (CH_2) (94.0)	13.1 (CH_3) (10.6)			

---

[a] In C_6D_6 (ca. 20%) at 27–28°C; δ values with respect to BF_3-OEt_2 (external), Me_4Sn (external), and Me_4Si (external, $\delta(^{13}C)$ (C_6D_6) 128.0); values $J(^{119}Sn^{13}C)$ are given in parentheses and (br) denotes the broad resonance of a boron-bonded ^{13}C nucleus. [b] Assignment might be reversed.

TABLE 2

^{11}B, ^{119}Sn AND ^{13}C NMR DATA[a] FOR STANNACYCLOPENTADIENES

	δ(^{119}Sn)	δ(^{11}B)	δ(^{13}C)										
			C(2)	C(3)	C(4)	C(5)	SnMe	BR	C(a)	C(b)[b]	C(c)	C(d)[b]	C(e)
 (8)													
8a, R = Me	3.0	79.0	140.9 (403.0)	172.7 (br)	169.9 (74.5)	122.2 (467.5)	−9.6 (333.3)	16.0 (br)	43.3 (65.9)	33.8	22.3	31.5	33.5 (br)
8b, R = Et	4.8	83.0	139.0 (405.3)	171.0 (br)	170.0 (75.7)	121.9 (470.0)	−9.7 (331.0)	23.6, 11.3 (br)	43.2 (67.2)	33.7	22.2	31.5	33.0 (br)
8c, R = i-Pr	4.3	81.0	138.0 (403.0)	171.4 (br)	170.8 (76.3)	122.7 (468.0)	−9.8 (332.0)	27.9, 21.0 (br)	43.7 (66.1)	33.9	22.5	32.0	31.9 (br)
 (9c)	4.3[c]	81.0	137.7 (394.2)	173.0 (br)	169.2 (76.3)	119.2 (483.2)	−9.5 (332.0)	[d]	48.3 (CH) (58.5)	23.7 (CH$_3$)			
	19.5	82.0	128.1 (408.2)	175.3 (br)	162.7 (89.5)	121.1 (482.3)	−9.4 (330.4)	21.3, 9.2 (br)	30.9 (CH$_2$) (63.2)	13.1 (CH$_3$)			

---

[a] See footnote *a* Table 1. [b] See footnote *b* Table 1. [c] Minor product accompanying **8c**; ^{119}Sn resonance may be below of that for **8c**. [d] Overlap with ^{13}C resonances of **8c** in the same region.

tadienes [4,5,8]; data for a similar compound prepared previously [4] are also included in Table 2.

Experimental

All experiments and all handling of the compounds were carried out in dry solvents under N_2. The alkynylstannanes **1** and **5** were prepared by published procedures [18]. Compound **1** was used as a solution in THF. The *B*-alkyl-9-borabicyclo[3.3.1]nonanes **2a,c** were obtained from the reaction between *B*-methoxy-9-BBN and lithium alkyls [19]. Compound **2b** [20] was available. NMR spectra were recorded on JEOL FX 90Q and Bruker WP 200 instruments (for conditions see Table 1). The 2-D spectra were recorded on a Bruker AC 200 spectrometer.

*9-Methyl-10(2-trimethylstannyl-(E)-ethylidene)-9-borabicyclo[3.3.$2^{1,5}$]decane (**3a**)*

A 50 ml two-necked flask, equipped with a magnetic stirrer bar and N_2-inlet was charged with 10 ml of a solution of **1** in THF (1.11 *M*), diluted with 30 ml of hexane then placed in a bath at −78°C. After addition of 1.6 g (11.6 mmol) of *B*-Me-9-BBN (**2a**) the mixture was warmed to RT then stirred for 30 min. The solvent was removed in vacuo and the residue fractionally distilled to give 2.9 g (82%) of a colourless, extremely air-sensitive liquid, b.p. 79–83°C/10^{-2} Torr. Found: C, 52.1; H, 8.7; $C_{14}H_{27}BSn$ calc: C, 51.8; H, 8.4%.

^1H NMR of **3a** (300 MHz in C_6D_6); $\delta(^1H)$ ($J(^{119}Sn^1H)$): 0.16 (s, (53.6) SnMe; 0.93, s, BMe; 1.2–2.3, m; 2.75, m, H(a); 6.65, s, (88.0) =CH.

The reaction between **1** and **2b** was carried out as described previously [7], and the products of the reaction between **1** and **2c** were characterized by NMR spectroscopy after removal of the solvents. Attempts to distill **3c** led to decomposition.

^1H NMR of **3c** (300 MHz in C_6D_6); $\delta(^1H)$ ($J(^{119}\mathrm{Snu1H})$): 0.17, s, (53.5) SnMe; 2.77, m, H(a); 6.60, s, (85.0) =CH.

*7-Alkyl-4,4-dimethyl-7-bora-4-stannatricyclo[6,3,$3^{1,8}$,$0^{2,6}$]tetradeca-2,5-dienes (**8a,b,c**)*

A solution of **5** (3 g, 15 mmol) in 60 ml of hexane was placed in a two-necked flask (magnetic stirrer bar, N_2-inlet) and cooled to −78°C. After addition of **2** (16.5 mmol, ca. 10% excess) the mixture was allowed to warm to RT then stirred for 3 h. The solvent was removed in vacuo from the light yellow solution to leave a yellow (**8b,c**) to brown (**8a**) viscous oil. NMR spectra showed that this material contained > 80% of **8**. Attempts to distil compounds **8a,b,c** at low pressure (10^{-4} Torr) led to extensive decomposition when the oil bath was heated to > 90°C. The excess of **2** was recovered, and a red-brown polymeric material was left in the flask.

^1H NMR of compounds **8** (300 MHz in C_6D_6); $\delta(^1H)$ ($J(^{119}Sn^1H)$): **8a**, 0.32, s, (57.0) SnMe, 3.2, m, H(a); 5.80, s, (160.0) H(5); 6.80, s, (161.0) H(2);
8b, 0.32, s, (57.0) SnMe; 3.2, m, H(a); 5.88, s, (161.1) H(5); 6.74, s, (160.2) H(2);
8c, 0.22, s, (57.6) SnMe; 3.2, m, H(a); 6.03, s, (158.0) H(5); 6.86, s, (160.0) H(2).

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for support of this work. We thank Prof. Dr. R. Köster for a gift of *B*-ethyl-9-BBN (**2b**).

References

1 S. Kerschl and B. Wrackmeyer, Z. Naturforsch. B, 41 (1986) 890.

2 (a) G.E. Herberich, G. Buller, B. Hessner and W. Oschmann, J. Organomet. Chem., 195 (1980) 249; (b) J.J. Eisch, J.E. Galle and S. Kozima, J. Am. Chem. Soc., 108 (1986) 379.

3 (a) R. Usón, J. Vincente and M.T. Chicote, Inorg. Chim. Acta, 35 (1979) L305; (b) R. Usón, J. Vincente and M.T. Chicote, J. Organomet. Chem., 209 (1981) 271; (c) A.J. Ashe, III, and F.J. Drone, Organometallics, 3 (1984) 495.

4 L. Killian and B. Wrackmeyer, J. Organomet. Chem., 132 (1977) 213.

5 L. Killian and B. Wrackmeyer, J. Organomet. Chem., 148 (1978) 137.

6 A. Schmidt and B. Wrackmeyer, Z. Naturforsch. B, 33 (1978) 855.

7 C. Bihlmayer and B. Wrackmeyer, Z. Naturforsch. B, 36 (1981) 1625.

8 S. Kerschl and B. Wrackmeyer, Z. Naturforsch. B, 39 (1984) 1037.

9 L. Killian and B. Wrackmeyer, J. Organomet. Chem., 153 (1978) 153.

10 R. Köster in R. Köster (Ed.), Organobor-Verbindungen I, in Houben-Weyl Methoden der Organischen Chemie. Vol. XIII/3a. G. Thieme Verlag, Stuttgart, 1982, pp. 322–324, and literature cited therein.

11 (a) B. Wrackmeyer, Z. Naturforsch. B, 33 (1978) 385; (b) B. Wrackmeyer and C. Bihlmayer, J. Chem. Soc. Chem. Commun., (1981) 1093.

12 B. Wrackmeyer, Organometallics, 3 (1984) 1.

13 (a) H. Nöth and B. Wrackmeyer, in P. Diehl, E. Fluck and R. Kosfeld (Eds.), NMR Spectroscopy of Boron Compounds, in NMR Basic Pronciples and Progress, Vol. 14, Springer Verlag, Berlin, 1978, pp. 1–461. (b) B. Wrackmeyer and R. Köster, in R. Köster (Ed.), Analytik der Organobor-Verbindungen, in Houben Weyl Methoden der Organischen Chemie, Vol. XIII/3c, G. Thieme Verlag, Stuttgart, 1984, pp. 377–611.

14 (a) B. Wrackmeyer, Revs. Silicon, Germanium, Tin, Lead Compds. 6 (1982) 75; (b) B. Wrackmeyer, Ann. Rep. NMR Spectrosc., 16 (1985) 73–186.

15 B. Wrackmeyer, Polyhedron, 5 (1986) 1709.

16 (a) A.A. Maudsley and R.R. Ernst, Chem. Phys. Lett. 50 (1977) 368; (b) R. Benn and H. Günther, Angew. Chem., 95 (1983) 381; Angew. Chem. Int. Ed. Engl., 22 (1983) 350.

17 J.K.M. Saunders and J.D. Mersh, Progr. NMR Spectrosc., 15 (1982) 353.

18 B. Wrackmeyer in R.B. King and J.J. Eisch (Eds.), Organometallic Syntheses, Vol. 3, Elsevier, New York, 1986, pp. 572–575.

19 G.W. Kramer and H.C. Brown, J. Organomet. Chem., 73 (1974) 1.

20 R. Köster and P. Binger, Inorg. Synth., 15 (1974) 141.