Reaction of 9-Borabicyclo[3.3.1]nonane with Alkyn-1-yltin Compounds. Molecular Structure of the 9-Propyn-1-yl-9-borabicyclo[3.3.1]nonane Pyridine Adduct

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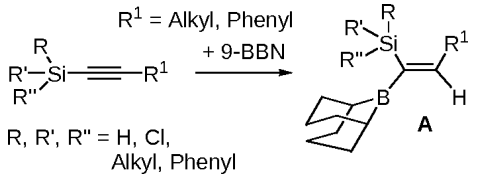
Trimethyl- and triethyl(propyn-1-yl)tin react with 9-borabicyclo[3.3.1.]nonane (9-BBN) mainly by exchange of the propynyl group against hydrogen, accompanied by numerous side reaction. This is in contrast to the findings for other alkynyltin compounds bearing a second bulky substituent at the C≡C bond. The exchange product, 9-propyn-1-yl-9-borabicyclo[3.3.1]nonane, was isolated as its crystalline pyridine adduct and fully characterised by NMR spectroscopy in solution and X-ray structural analysis in the solid state.

Key words: Alkynyltin Compounds, 9-BBN, Exchange, NMR, X-Ray

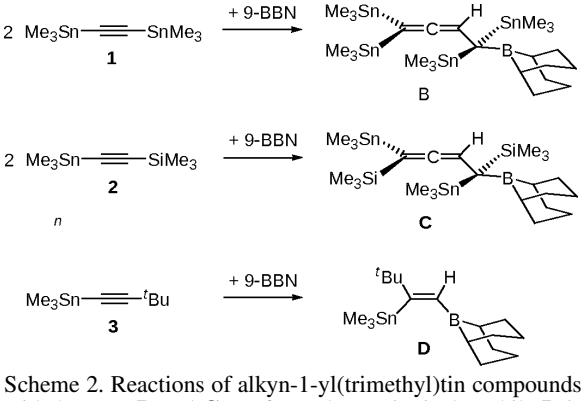
Introduction

With few exceptions [1], alkyn-1-ylsilanes react with dialkylboron hydrides in the usual way by 1,2-hydroboration [2, 3] to give selectively various 1-siyl-1-dialkylboryl-alkenes of type **A**, fairly independent of the nature of substituents R, R′ and R″ at silicon, as we have shown for numerous examples [4, 5] (Scheme 1).



Scheme 1. 1,2-Hydroboration of alkyn-1-ylsilanes with 9-BBN.

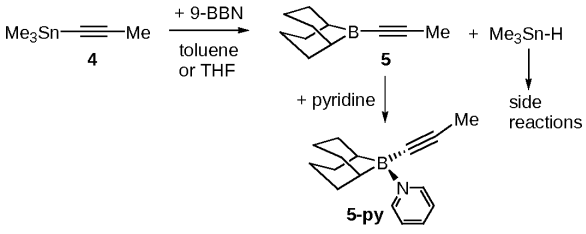
In this context, the reactivity of the hydroborating reagents, such as 9-borabicyclo[3.3.1]nonane (9-BBN), towards alkyn-1-yltin compounds is of interest. Previous studies have indicated that 1,2-hydroboration of the C≡C bond in alkyn-1-yltin compounds may be the exception rather than the rule [6, 7]. Thus alkyn-1-yltin compounds like **1**, **2** or **3** react with 9-BBN (Scheme 2) to give allenes (**B**, **C**) or an alkene derivative (**D**), respectively, all of which can be considered as the result of 1,1-hydroboration [6]. In further work, the allenes were characterised by X-ray structural analysis [8].



Scheme 2. Reactions of alkyn-1-yl(trimethyl)tin compounds with 9-BBN: **B** and **C** are formed quantitatively, while **D** is formed and isolated in low yield.

Results and Discussion

Since the bulkiness of the substituents at the C≡C bond in **1**, **2** or **3** might have an influence on the reactivity and product distribution, we have now studied the reaction of trimethyl(propyn-1-yl)tin (**4a**) and triethyl(propyn-1-yl)tin (**4b**) with 9-BBN (Scheme 3). According to ^{11}B and ^{119}Sn NMR spectra of the reaction mixtures, the reaction proceeded mainly by exchange of the propynyl group against hydrogen, ac-



Scheme 3. Reaction of trimethyl(propyn-1-yl)tin with 9-BBN.

companied or followed by extensive decomposition. The solvent (THF or toluene) did not affect the reaction, except that it took longer in toluene because of the low solubility of 9-BBN in this solvent. The ^{119}Sn NMR spectra revealed a signal of appreciable intensity for Me_3Sn–H or Et_3Sn–H (δ^{119}Sn = −104.5 or −50 [9]) only in the first minutes after starting the reaction. Apparently both trimethyl- or triethyltin hydride are rapidly consumed in side reactions. The ^{11}B NMR spectra showed a signal for 9-propyn-1-yl-9-borabicyclo[3.3.1]nonane **5** as the THF adduct [10, 11] (δ^{11}B = 10.6) or as the free borane in toluene (δ^{11}B = 73.0). These signals were strong after the reaction of **4a** and weak after the reaction of **4b**. In the case of **4a**, addition of pyridine to the reaction solution in THF afforded the pyridine adduct **5-py** which readily crystallised from the mixtures and could be isolated. For reactions starting from **4b**, the ^{119}Sn NMR spectra indicated the presence of numerous unidentified products, and no attempt was made to isolate **5-py**.

The previous results (Scheme 2) have been indicative of a zwitterionic borate-like intermediate **E**, well known from 1,1-organoboration reactions [12, 13]. In the cases of **1**, **2**, and **3**, the bulkiness of the Me_3Sn, Me_3Si or ^{t}Bu group, respectively, stabilises this intermediate sufficiently to allow for 1,1-hydroboration instead of exchange. In the cases of **1** and **2**, 1,1-hydroboration is fast when compared with exchange because of the reactivity of the Sn–C(alkyne) and Si–C(alkyne) bonds. In the case of **3**, however, obviously exchange competes successfully with 1,1-hydroboration, since the formation of Me_3Sn–H was observed [6], even more readily than in the present study of **4a**. In the cases of **4a**, **b**, studied here, exchange is faster than 1,1-hydroboration. The ^{119}Sn NMR spectrum of the reaction mixture containing **4b** and 9-BBN in THF showed in the first minutes after warming the sample to ambient temperature a broad signal at rather high frequency (δ^{119}Sn = +134.0) in the region conceivable [13] for an intermediate **E**. It is remarkable that there is no example of an alkyn-1-yltin compound known so far, for which straightforward 1,2-hydroboration has been observed.

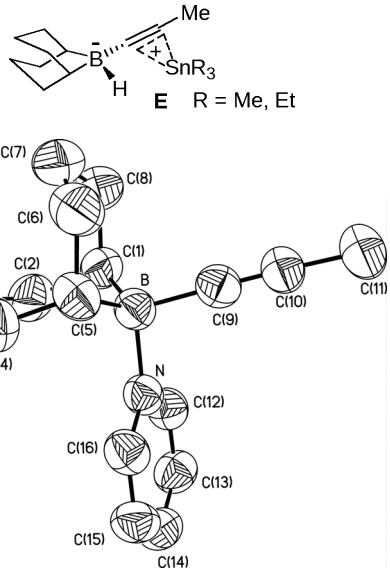


Fig. 1. Molecular structure of **5-py** (ORTEP, 40 % probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (pm) and angles (deg): N–B 166.2(4), N–C(16) 134.7(3), N–C(12) 134.9(3), B–C(9) 160.6(4), B–C(1) 162.2(4), B–C(5) 160.9(4), C(1)–C(2) 153.7(4), C(1)–C(8) 154.2(4), C(9)–C(10) 120.9(4), C(10)–C(11) 146.9(4); C(5)–B–C(1) 105.2(2), N–B–C(9) 102.4(2), B–C(9)–C(10) 178.5(3), C(9)–C(10)–C(11) 178.6(4), C(12)–N–C(16) 117.1(3).

The structure of **5-py** in solution follows conclusively from the consistent set of NMR data (Experimental). The N–B coordination is strong because ^{13}C(CH_2) resonances are observed as pairs as required for a rigid structure. In addition, the ^{13}C NMR spectra show that exchange with an excess of pyridine is slow on the NMR time scale. The ^{13}C(pyridine) NMR signals are broadened because of slow rotation about the B–N bond. In contrast, the incomplete set of ^{13}C NMR data reported for the THF adduct of **5** [10] can be interpreted as the result of THF exchange at the boron atom.

In the solid state of **5-py** (see Fig. 1), the bicyclic structure is typical of 9-BBN derivatives [14 – 16]. The boron atom is in distorted tetrahedral surroundings, and all bond lengths and angles are in the expected range. This is also true for the propynyl group and the pyridine ligand.

Experimental Section

All preparations and the handling of samples were carried out under inert atmosphere (Ar) and in carefully dried solvents, and oven-dried glassware was used. Starting materials such as 9-BBN, trimethyl- and triethyltin chloride, ^{n}BuLi (1.6 M in hexane) and propyne were used as commercial products. The propyn-1-yltin compounds **4a**, **b** were prepared following literature methods [17, 18]. NMR spectra were measured at 23 °C from samples in 5 mm (o. d.) tubes in THF or in toluene using Bruker WP 200 and Varian Inova 300 and 400 NMR spectrometers, equipped with multinuclear units. Chemical shifts were given as follows: δ^1H(C_6D_5H) = 7.15, δ^{13}C(C_6D_6) = 128.0, δ^{11}B(BF_3–OEt_2) = 0 for $\Xi(^{11}B)$ = 32.083971 MHz, δ^{119}Sn($SnMe_4$) = 0 for $\Xi(^{119}Sn)$ = 37.290665 MHz. ^{119}Sn NMR spectra were recorded using the refocused INEPT pulse sequence with ^{1}H decoupling [9, 19].

*Reaction of the propyn-1-yltin compounds **4a, b** with 9-BBN*

Trimethyl- (**4a**) or triethyl(propyn-1-yl)tin (**4b**) (1.9 mmol) and 9-BBN (0.23 g, 1.9 mmol) were mixed in THF or toluene (5 mL) at −78 °C, and the reaction mixtures were warmed to ambient temperature and kept stirring. The progress of the reactions was monitored by measuring ^{11}B and ^{119}Sn NMR spectra. In the case of **4a** in THF, a few drops of pyridine were added at r. t. after 2 h, and crystalline **5-py** (m. p. 119 °C) was obtained after 3 – 4 h. Crystals suitable for single crystal X-ray diffraction were grown from C_6D_6 solutions of **5-py**, and contained a half equivalent of C_6D_6. The toluene solutions were kept stirring for 2 d, until solid 9-BBN was consumed. **5-py**: ^{1}H NMR (400 MHz in C_6D_6): δ^1H = 1.85 – 1.1 (m, 14H, 9-BBN), 1.99 (s, 3H, ≡C-Me), 7.65, 8.05, 8.55 (br, m, 5H, pyridine). – ^{13}C NMR (100.5 MHz in C_6D_6): δ^{13}C = 5.2 (Me), 25.0, 25.6, 33.1, 33.9 (CH_2), 27.0 (br, BCH), 100.5 (br, B–C≡), 90.1 (≡C), 124.5, 138.5, 145.8 (pyridine). – ^{11}B NMR (128.4 MHz in C_6D_6): δ^{11}B = −3.2.

*X-Ray structural analysis of **5-py***

The X-ray crystal structural analysis of **5-py** was carried out on a single crystal sealed in a Lindemann capillary at 293(2) K using a Stoe IPDS II system; λ = 0.71069 Å, formula weight = 278.21, crystal system monoclinic, space group $C2/c$, unit cell dimensions: a = 19.138(4), b = 8.2876(17), c = 22.083(4) Å, β = 102.23(3)°, volume = 3423.1(12) Å^3, Z = 8, μ(MoK_α) = 0.061 mm^{-1}, F(000) = 1208 e. Crystal size: 0.22 × 0.18 × 0.16 mm^3, ϑ range for data collection: 2.18 – 26.16°, index ranges: $-23 \le h \le 23$, $-10 \le k \le 10$, $-27 \le l \le 27$, reflections collected: 11599, independent reflections: 3351, R_{int} = 0.0934, completeness to ϑ_{max} = 25.15° : 97.8 %, data/restraints/parameters: 3351 / 0 / 190, goodness-of-fit on F^2: 0.812, final R indices [$I \ge 2\sigma(I)$]: $R1$ = 0.0573, $wR2$ = 0.1342, R indices (all data): $R1$ = 0.1538, $wR2$ = 0.1621, $\Delta\rho_{fin}$ (max/min): 0.147/−0.175 e Å^{-3}. Structure solution and refinement were accomplished using SHELX-97 [20].

CCDC 717781 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) B. Wrackmeyer, O. L. Tok, M. H. Bhatti, S. Ali, *Z. Naturforsch*. **2003**, *58b*, 133; b) B. Wrackmeyer, H. E. Maisel, W. Milius, M. H. Bhatti, S. Ali, *Z. Naturforsch*. **2003**, *58b*, **543**.

[2] H. C. Brown, *Organic Synthesis via Boranes*, Wiley, New York, **1975**.

[3] a) J. A. Soderquist, J. C. Colberg, L. DelValle, *J. Am. Chem. Soc*. **1989**, *111*, 4873; b) K. Uchida, K. Utimoto, H. Nozaki, *J. Org. Chem*. **1976**, *41*, 2941; c) K. Uchida, K. Utimoto, H. Nozaki, *Tetrahedron* **1977**, *33*, 2987; d) N. G. Bhat, A. Garza, *Tetrahedron Lett*. **2003**, *44*, 6833.

[4] B. Wrackmeyer, W. Milius, M. H. Bhatti, S. Ali, *J. Organomet. Chem*. **2003**, *669*, 72.

[5] a) B. Wrackmeyer, E. Khan, R. Kempe, *Z. Naturforsch*. **2007**, *62b*, 75; b) B. Wrackmeyer, E. Khan, S. Bayer, K. Shahid, *Z. Naturforsch*. **2007**, *62b*, 1174; c) B. Wrackmeyer, E. Khan, W. Milius, *Z. Naturforsch*. **2008**, *63b*, 1267.

[6] B. Wrackmeyer, C. Bihlmayer, *J. Chem. Soc., Chem. Commun*. **1981**, 1093.

[7] B. Wrackmeyer, C. Bihlmayer, M. Schilling, *Chem. Ber*. **1983**, *116*, 3182.

[8] B. Wrackmeyer, U. Dörfler, G. Kehr, H. E. Maisel, W. Milius, *J. Organomet. Chem*. **1996**, *524*, 169.

[9] a) B. Wrackmeyer, *Annu. Rep. NMR Spectrosc*. **1999**, *38*, 203; b) B. Wrackmeyer in *Tin Chemistry – Fundamentals, Frontiers and Applications* (Eds.: A. Davies, M. Gielen, K. Pannell, E. Tiekink), Wiley, Chichester, **2008**, p. 17.

[10] a) H. Feulner, N. Metzler, H. Nöth, *J. Organomet. Chem*. **1995**, *489*, 51; b) the δ^{11}B value of **5-THF** in THF (δ = 19.5) given in this work [10a] does not agree with our measurements and is also in contrast with related data given in [11].

[11] H. C. Brown, J. A. Sinclair, *J. Organomet. Chem*. **1977**, *131*, 163.

[12] B. Wrackmeyer, *Coord. Chem. Rev*. **1995**, *145*, 125.

[13] B. Wrackmeyer, S. Kundler, R. Boese, *Chem. Ber*. **1993**, *126*, 1361.

[14] a) D. J. Brauer, C. Krüger, *Acta Crystallogr. B* **1973**, *29*, 1684; b) M. Yalpani, R. Boese, R. Köster, *Chem. Ber*. **1988**, *121*, 287; c) M. Yalpani, R. Boese, R. Köster, *Chem. Ber*. **1990**, *123*, 1285.

[15] a) R. Köster, G. Seidel, D. Blaeser, R. Boese, *Z. Naturforsch* **1994**, *49b*, 370; b) B. Wrackmeyer, H. E. Maisel, W. Milius, A. Badshah, E. Molla, A. Mottalib, *J. Organomet. Chem*. **2000**, *602*, 45; c) B. Wrackmeyer, B. Schwarze, W. Milius, *J. Organomet. Chem*. **1995**, *489*, 201; d) B. Wrackmeyer, E. Khan, R. Kempe, *Z. Anorg. Allg. Chem*. **2007**, *633*, 453.

[16] X. Chen, S. Liu, C. E. Plecnik, F.-C. Liu, G. Fraenkel, S. G. Shore, *Organometallics* **2003**, *22*, 275; b) W. J. Evans, S. E. Lorenz, J. W. Ziller, *Chem. Commun*. **2007**, 4662; c) E. Ding, B. Du, F.-C. Liu, S. Liu, E. A. Meyers, S. G. Shore, *Inorg. Chem*. **2005**, *44*, 4871.

[17] a) W. E. Davidsohn, M. C. Henry, *Chem. Rev*. **1967**, *67*, 73; b) L. Brandsma, *Synthesis of Acetylenes, Allenes, and Cumulenes – Methods and Techniques*, Elsevier, Amsterdam, **2004**.

[18] M. L. Quan, P. Cadiot, *Bull. Soc. Chim. France* **1965**, 35.

[19] a) G. A. Morris, R. Freeman, *J. Am. Chem. Soc*. **1979**, *101*, 760; b) G. A. Morris, *J. Am. Chem. Soc*. **1980**, *102*, 428.

[20] G. M. Sheldrick, SHELXS/L-97 (release 97-2), Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1998**.