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Reaction of 1-alkynylsilanes with triallylborane—competition between 1,1- and 1,2-allylboration

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Abstract

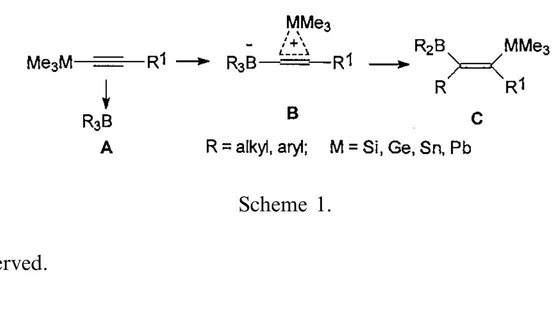
The reaction of triallylborane (All_3B, **1**) with various 1-alkynylsilanes of the type $Me_3Si{-}C{\equiv}CR^1$ [R^1 = H (**2a**), Me (**2b**), Ph (**2c**), $C{\equiv}C{-}SiMe_3$ (**2d**), $SiMe_3$ (**2e**)], $Ph_3Si{-}C{\equiv}CPh$ (**3**) $MeC{\equiv}C{-}SiMe_2SiMe_2{-}C{\equiv}CMe$ (**4**) and $Me_2Si(Cl){-}C{\equiv}CPh$ (**5**) was studied. Triallylborane **1** turned out to be much more reactive than other triorganoboranes R_3B (e.g. R = Et, Ph). In the cases of **2** and **5**, the products are organometallic-substituted alkenes **6** and **11**, respectively, with the boryl and silyl group in *cis*-positions as the result of selective 1,1-allylboration (via cleavage of the Si–C≡ bond) or mixtures of such and other alkenes **7** or **8** because of competition between 1,1- and 1,2-allylboration (the composition of these mixtures depends on the polarity of the solvent). In the case of **4**, the 1,2-dihydro-1,2-disilaborepine derivative **12** is formed selectively (twofold 1,1-allylboration). The alkyne **3** did not react with **1**. The products were characterised by ^{1}H-, ^{11}B-, ^{13}C- and ^{29}Si-NMR spectroscopy.

Keywords: Silicon; Boron; Triallylborane; Alkenes; Alkynes; 1,1-Allylboration; 1,2-Allylboration; NMR

1. Introduction

1-Alkynylsilanes are readily available by standard preparative procedures [1], and much of their synthetic potential can be exploited by taking advantage of the reactivity of the C≡C and/or the Si–C≡ bond. Recently it was shown that triorganoboranes R_3B react with 1-alkynylsilanes by cleavage of the Si–C≡ bond, accompanied by 1,1-organoboration [2]. These reactions require heating up to $>100°C$ for several hours or days and lead selectively to organometallic-substituted alkenes [3], to siloles [4,5] and other heterocycles [6,7]. The principal mechanism of such 1,1-organoboration reactions is fairly well understood [2]: the reaction is supposed to start with a weak interaction as indicated in **A**, from which a stronger interaction leads to a borate-like intermediate by partial cleavage of the Si–C≡ bond (**B**) and finally to the alkenes of type **C** (Scheme 1). In the case of certain 1-alkynyltin or -lead compounds, it proved possible to isolate such zwitterionic intermediates corresponding to **B** and characterise them by X-ray structural analysis [8].

Owing to permanent allylic rearrangement, triallylborane (All_3B, **1**) possesses unique properties among triorganoboranes and its great synthetic potential in reactions with unsaturated substrates has been well documented [9]. In the case of alkynes a weak interaction like in **A** is conceivable, followed in general by



Scheme 1.

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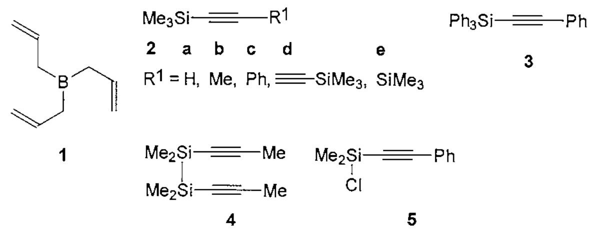
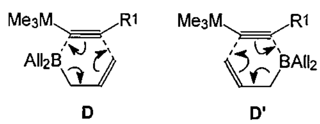


Scheme 2.

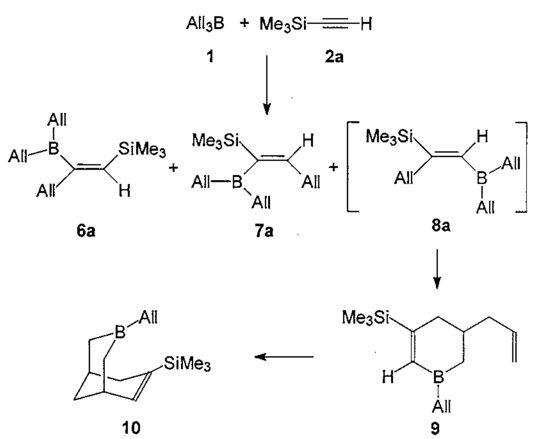
1,2-allylboration for which a six-membered cyclic transition state **D** has been proposed [9,10]. However, the reactivity of **1** towards 1-alkynylsilanes has never been studied in detail. An early report has claimed that **1** reacts with ethynyltrimethylsilane **2a** exclusively by 1,2-allylboration [11]. In a first more systematic attempt, we have now used NMR spectroscopy to investigate the products obtained from the reaction of **1** with various 1-alkynylsilanes **2**–**5** (Scheme 2).



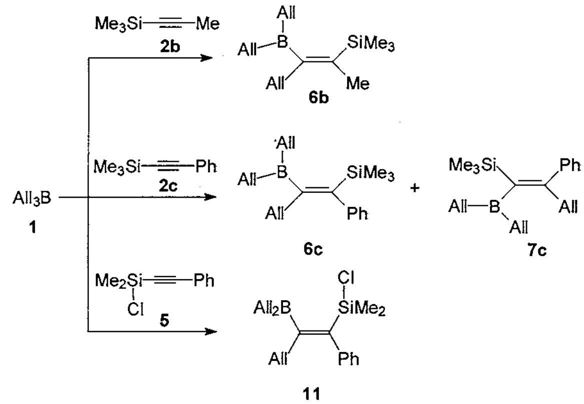
2. Results and discussion

2.1. Reactions of 1 with the 1-alkynylsilanes 2, 3 and 5

In contrast to triethylborane, triallylborane reacts with most 1-alkynylsilanes already at room temperature. However, the reaction is less selective because of competition between 1,1- and 1,2-allylboration. This is shown in Scheme 3 for the reaction of **1** with **2a**. Three products **6a**, **7a** and **9** are formed in a ratio of 2:1:1, where **7a** and **9** arise from 1,2-allylboration. The compound **9** results from fast rearrangement of **8a** (not detected in solution), and this type of compound was observed only for $R^1 = H$. The heterocycle **9** rearranges slowly to the bicyclic compound **10**. This sequence of reactions has been described for numerous other terminal alkynes when treated with triallylborane [9]. If the reaction is carried out in an non-polar solvent (pentane), the amount of **6a** is reduced with respect to **7a** and **9**.



Scheme 3.



Scheme 4.

Scheme 4 summarises the results of the reaction of **1** with the alkynes **2b**, **c** and **5**. Interestingly, **6b** is formed selectively by 1,1-allylboration. In the case of **2c**, the reaction with **1** in $CHCl_3$ affords a 2:1 mixture of **6c** and **7c**, whereas a 1:1 mixture is obtained if pentane serves as solvent. The reaction of **1** with **5** also proceeds slowly at room temperature via 1,1-allylboration to give **11**. Previously it has been found that triethylborane does not react with 1-alkynylsilanes of the type **5**, even after heating for several days at 100°C [7].

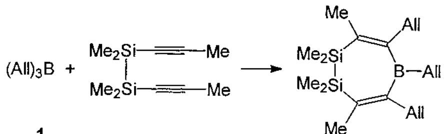
Triallylborane **1** reacts with **2d** via 1,1-allylboration to give **6d** after heating to 100°C in toluene. However, the conversion amounts only to ca. 10%. For comparison, triethylborane does not react at all with **2d**, and it has been noted that the corresponding alkene, prepared via a different route, decomposes into Et_3B and **2d** upon heating to > 140°C [12].

By increasing the bulkiness of groups attached to the Si atom, as in **3**, the reactivity decreases. Thus, we did not observe any reaction between **1** and **3**, even after prolonged heating of the mixture at 100°C.

2.2. Reaction of 1 with 1,1,2,2-tetramethyl-1,2-di-1-propynyl-disilane 4

The alkyne **4** is known to react with various triorganoboranes (e.g. Et_3B, Ph_3B) by heating to 100°C to give selectively 1,2-dihydro-1,2-disilaborepine derivatives [6], and the molecular structure of the compound derived from Ph_3B has been determined [6b]. In an analogous manner, however already at room temperature, the reaction of triallylborane **1** affords quantitatively and selectively the seven-membered heterocycle

12 as a result of consecutive inter- and intramolecular 1,1-allylborations.



1 4 12

2.3. Mechanistic implications

The 1,2-allylboration to **8a**, with a transition state **D′**, appears to be a special case, and is probably kinetically controlled owing to $R^1 = H$. For all other products, the question of differences between the intermediate of type **B** and the transition state **D** arises. **B** is more polar and should be preferred in a polar solvent, which is supported by the experimental evidence that 1,1-allylboration products are favoured if the reactions are carried out in chloroform instead of pentane.

Why is triallylborane more reactive than other triorganoboranes? In comparison with trialkylboranes, triallylborane is a stronger Lewis acid as shown by the stability of complexes with pyridine derivatives [13]. Therefore, it is conceivable that the interaction in **A** is stronger for triallylborane than for trialkylboranes, and further reactions take place more readily. On the other hand, triphenylborane, which must be regarded as a stronger Lewis acid than triallylborane, is less reactive towards 1-alkynylsilanes than triallylborane (compare reaction conditions in Section 2.2 and those reported in Refs [3,6,7]). Hence, the nature of the allyl groups plays an important role once the interaction between boron and the C≡C bond in **A** is sufficiently strong.

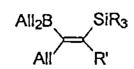
2.4. NMR-spectroscopic results

The structural assignments are based on consistent sets of ^{1}H-, ^{13}C- and ^{29}Si-NMR data (Table 1). ^{11}B chemical shifts are all found in the typical range for these types of triorganoboranes [14]. The characteristically broadened ^{13}C-NMR signals for boron-bonded carbon atoms (scalar relaxation of the second kind [15]) help to assign the carbon framework. The latter is further established by observation of ^{29}Si satellites corresponding to $J(^{29}Si,^{13}C)$. These parameters can also be measured in the ^{29}Si-NMR spectra (see Fig. 1), serving for mutual assignments of ^{13}C- and ^{29}Si-NMR signals. There is a distinctive broadening in the ^{29}Si-NMR signals if ^{11}B nuclei are in *cis*, *trans* or *geminal* positions, as has been noted previously [16] and has been ascribed to partially relaxed scalar ^{29}Si–^{11}B coupling. The proposed stereochemistry of the products is also supported by appropriate experiments for ^{1}H/^{1}H-NOE difference spectroscopy [17].

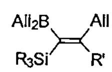
3. Conclusions

Triallylborane is much more reactive towards 1-alkynylsilanes than triethylborane. Cleavage of the Si–C≡ bond, the essential step in 1,1-allylboration, takes place already at room temperature. In some cases, the well-known 1,2-allylboration competes with 1,1-allylboration. However, in most cases 1,1-allylboration is dominant, in particular in more polar solvents. Owing to the reactive Si–Cl bond, **11** is an attractive starting material for further transformations. The borepine derivative **12** is an example of a new polyene with five non-conjugated double bonds in one molecule obtained by a one-pot reaction of a simple alkyne with triallylborane.

Table 1
^{11}B-, ^{13}C- and ^{29}Si-NMR data[a] of the alkenes **6, 7, 11, 12**



Compound	δ ^{13}C (B–C=)	δ ^{13}C (Si–C=)	δ ^{13}C(SiMe)	δ ^{29}Si
6a [b]	165.0 (9.1)	129.2 (67.9)	−0.4 (51.5)	−9.3
6b [c]	154.7	134.0 (68.5)	−0.9 (50.5)	−5.2
6c [d]	157.2	143.3 (64.9)	−0.6 (51.9)	−6.8
11 [e]	151.6	143.9 (n.m.)	4.6 (58.6)	14.1
12 [f]	158.9	135.7 (n.m.)	−2.5 (43.5)	−23.9



	δ ^{13}C (B(Si)–C=)	δ ^{13}C (All–C=)	δ ^{13}C (SiMe)	δ ^{29}Si
7a [g]	155.1	136.5 (8.8)	−0.2 (51.8)	−7.9
7c [h]	151.2	143.9 (n.m.)	0.9 (51.9)	−14.8

[a] In $CDCl_3$ at 20°C; coupling constants $J(^{29}Si,^{13}C) \pm 0.3$ Hz are given in parentheses; n.m. means not measured; br. denotes a broad signal of acarbon atom linked to boron; δ ^{11}B 82 = 1, except for **12** with δ ^{11}B 72.0.

[b] Other δ ^{13}C data: 34.0 (br., CH_2B); 43.1 (CH_2); 114.2 (=CH_2); 116.4 (=CH_2); 135.5 (–CH=); 136.6 (–CH=).

[c] Other δ ^{13}C data: 16.1 (CH_3); 34.0 (CH_2); 36.1 (br., CH_2B); 113.8 (=CH_2); 115.6 (=CH_2); 135.2 (–CH=); 136.6 (–CH=).

[d] Other δ ^{13}C data: 36.7 (br., CH_2B); 37.0 (CH_2); 114.4 (=CH_2); 115.8 (=CH_2); 127.6 (Ph); 128.2 (Ph); 128.8 (Ph); 134.9 (–CH=); 136.3 (–CH=); 145.0 (Ph).

[e] Other δ ^{13}C data: 36.5 (br., CH_2B); 47.4; 113.9 (=CH_2); 117.4 (=CH_2); 127.4 (Ph); 127.9 (Ph); 128.4 (Ph); 134.7 (–CH=); 136.6 (–CH=).

[f] Other δ ^{13}C data: 16.3 (CH_3); 35.0 (CH_2); 37.5 (br., CH_2B); 113.7 (=CH_2); 115.4 (=CH_2); 136.0 (–CH=); 136.4 (–CH=).

[g] Other δ ^{13}C data: 36.1 (br., CH_2B); 41.0 (CH_2); 113.6 (=CH_2); 116.9 (=CH_2); 136.3 (–CH=); 137.4 (–CH=).

[h] Other δ ^{13}C data: 36.5 (br., CH_2B); 48.5 (CH_2); 113.8 (=CH_2); 116.9 (=CH_2); 126.6 (Ph); 132.0 (Ph); 135.6 (–CH=); 136.3 (Ph); 136.7 (–CH=); 148.5 (Ph).

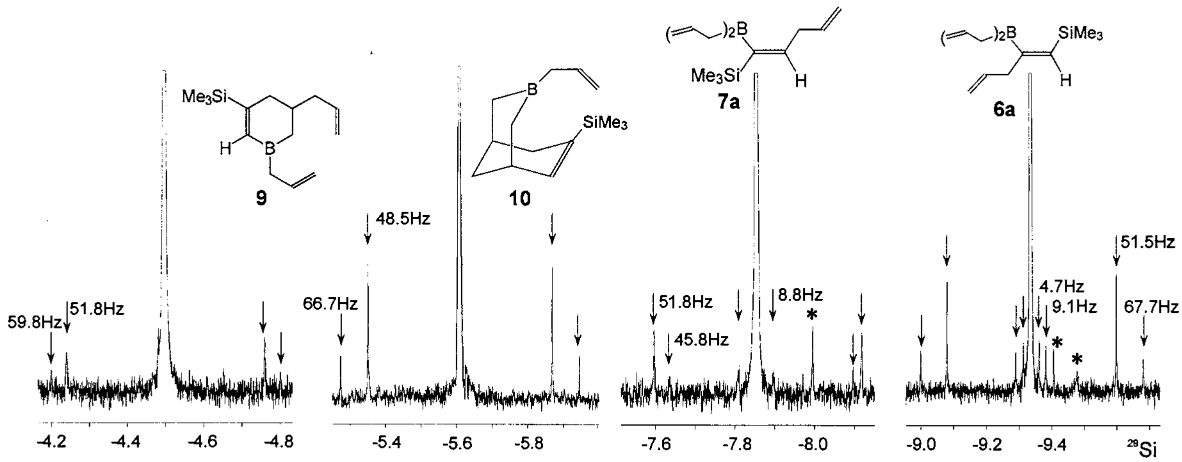


Fig. 1. 99.4 MHz ^{29}Si-NMR signals of the mixture containing the products **6a**, **7a**, **9** and **10** of the reaction of **1** with **2a** (impurities are marked by asterisks). Although all ^{29}Si-NMR signals (except in the case of **10**) are markedly broadened by partially relaxed scalar ^{29}Si–^{11}B coupling, it proved possible to observe ^{13}C satellites, which are marked by arrows (isotope-induced chemical shifts $^{1}\Delta^{12/13}$C(^{29}Si) will be discussed elsewhere). Their relative intensities serve for the assignment to $^{1}J(^{29}Si,^{13}C_{Me})$ and $^{1}J(^{29}Si,^{13}C=)$, and in the cases of **6a** and **7a**, the ^{13}C satellites due to $^{n}J(^{29}Si,^{13}C)$ ($n = 2,3$) are also resolved.

4. Experimental

The synthesis of all compounds was carried out in an atmosphere of dry argon, and carefully dried solvents were used throughout. Starting materials were either used as commercial products without further purification (Chlorosilanes, butyl lithium 1.6 M in hexane) or prepared as described (alkynylsilanes **2**, **3**, **5** [1], **4** [6a,b], All_3B (**1**) [18]). NMR measurements: Bruker ARX 250 or DRX 500 [^{1}H-, ^{11}B-, ^{13}C-, ^{29}Si-NMR (refocused INEPT [19] based on $^{2}J(^{29}Si,^{1}H) = 7$ Hz). Chemical shifts are given with respect to Me_4Si [$\delta^{1}H$ ($CHCl_3/CDCl_3$) = 7.24; $\delta^{13}C$ ($CDCl_3$) = 77.0; $\delta^{29}Si = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz], BF_3–OEt_2 [$\delta^{11}B = 0$; $\Xi(^{11}B) = 32.083971$ MHz]. Assignments are based on 2D ^{1}H/^{1}H-COSY, ^{1}H/^{13}C- and ^{1}H/^{29}Si-HETCOR experiments.

*4.1. Reaction of the 1-alkynylsilanes **2–5** with triallylborane **1**: general procedure*

To a solution of **2–5** (about 1 mmol) in 2 ml of $CDCl_3$ or pentane the equimolar amount of All_3B was added in one portion at room temperature. The progress of the reactions was monitored by ^{1}H- and ^{29}Si-NMR spectroscopy. Since most of these products undergo further rearrangements [9] upon heating, separation or purification by fractional distillation is not successful. However, several products such as **6b**, **11** and **12** are formed selectively in high purity and can be used for further transformations. All compounds are left as colourless, extremely air- and moisture-sensitive oils.

6a: ^{1}H-NMR: $\delta^{1}H = 5.8$–6.0, 4.8–4.9, 2.27 10H, All_2B; 5.7–5.8, 4.9–5.1, 2.83 5H, All; 5.69 1H, =C–H; 0.01 9H, Me_3Si.

6b: ^{1}H-NMR: $\delta^{1}H = 5.94$, 5.02, 4.89, 2.21 10H, All_2B; 5.70, 5.03, 4.91, 2.81 5H, All; 1.75 3H, Me; 0.01 9H, Me_3Si.

6c: ^{1}H-NMR: $\delta^{1}H = 7.52$, 7.36, 7.02 5H, Ph; 6.11, 5.02, 2.39 10H, All_2B; 5.57, 5.00, 2.74 5H, All; 0.04 9H, Me_3Si.

7a: ^{1}H-NMR: $\delta^{1}H = 5.8$–6.0, 4.8–4.9, 2.18 10H, All_2B; 5.7–5.8, 4.9–5.1, 2.67 5H, All; 5.84 (t, $J = 5.9$ Hz) 1H, =C–H; 0.09 9H, Me_3Si.

7c: ^{1}H-NMR: $\delta^{1}H = 7.35$–7.15 5H, Ph; 6.11, 5.05–4.85, 2.39 10H, All_2B; 5.72, 5.05–4.85, 2.94 5H, All; – 0.14 9H, Me_3Si.

10: ^{1}H-NMR: $\delta^{1}H = 6.00$ 1H, H-7; 5.91, 5.1–4.9, 2.05 5H, All; 2.46 1H, H-6; 2.40 1H, H-1; 2.32 1H, H-8; 1.87 1H, H-2; 1.79 1H, H-9; 1.71 1H, H-3; 1.61 1H, H-4; 1.46 1H, H-10; 1.17 1H, H-11; 1.06 1H, H-5; 0.13 9H, Me_3Si.

11: ^{1}H-NMR: $\delta^{1}H = 7.4$–7.1 5H, Ph, 6.12, 5.05, 2.38 10H, All_2B; 5.65, 4.95, 2.90 5H, All; 0.13 6H, Me_2Si.

12: ^{1}H-NMR: $\delta^{1}H = 5.88$, 4.89, 2.29 5H, AllB; 5.73, 5.02, 2.98 10H, All; 1.78 6H, Me; 0.14 12H, Me_2Si.

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