1,1-Ethylboration of Diethynyl(dimethyl)silane:  
Formation of a Silole Followed by [4+2] Cycloadditions to  
7-Silanorbornadienes and 7-Silanorbornenes

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1,1-Organoboration, Ethynylsilanes, Cy cloaddition, NMR Data

Diethynyl(dimethyl)silane, Me₂Si(C≡C-H)₂ 2, reacts with triethylborane, Et₃B 1, by 1,1-ethylboration to give a silole, 3-diethylboryl-4-ethyl-1,1-dimethyl-sila-2,4-cyclopentadiene 3, as a short-lived intermediate which reacts further with 2 or dimerizes via [4+2] cycloadditions to the 7-silanorbornadiene 4 or the 7-silanorbornene derivatives 5, respectively. Since the silole 3 was not detected by NMR, the analogous reactions were studied using 1-alkynyl(ethyl)dimethylsilanes, Me₂Si(C≡C-H)C≡C-R 6 (R = Bu (a), 'Pent (b), 'Bu (c)). In these cases, 1,1-ethylboration gave the siloles 7a,b,c and 7 7a,b,c now detected in the reaction solutions, and also 7-silanorbornadienes as [4+2] cycloaddition products. Major products were identified, and the progress of the reactions was monitored by NMR spectroscopy (¹H, ¹¹B, ¹³C and ²⁹Si NMR).

Introduction

Reactions of bis(1-alkynyl)ilanes with triorganoboranes have been shown to offer efficient routes to sila-2,4-cyclopentadienes (siloles) [1 - 3]. Indeed, this method appears more versatile than most other related preparative pathways [4]. Although silanes with a large variety of alkynyl groups, identical or different, linked to silicon have been studied in 1,1-organoboration reactions, ethynylsilanes have not received much attention so far, since complex mixtures of products were formed which were difficult to analyse [5]. Preliminary experiments with diethynyl(dimethyl)silane, Me₂Si(C≡C-H)₂ 2, and triethylborane, Et₃B 1, did not produce a silole [5]. Therefore, we have reinvestigated in more detail this reaction, using in particular ²⁹Si NMR spectroscopy. For comparison, the reactions of 1-alkynyl(ethyl)dimethylsilanes, Me₂Si(C≡C-H)C≡C-R (R = Bu (6a), 'Pent (6b), 'Bu (6c)), with 1 are also discussed.

Results and Discussion

General

Bis(1-alkynyl)silanes usually react with triorganoboranes by cleavage of one of the Si-C≡C bonds and 1,1-organoboration to give intermediates A in equilibrium with B, and the latter can rearrange by an intramolecular vinylboration to the silole D (Scheme 1; the reaction of triethylborane is shown). Zwitterionic intermediates of type B have been characterised for the lead and tin analogues [6, 7]. In the case of alkynylsilanes, the rather harsh reaction conditions (ca. 100 °C for several days) which are required to induce the intermolecular 1,1-organoboration leading to A, prevent in general the isolation or even the detection of intermediates of type A or B.

Thus, the success of the silole synthesis (D) depends on the stability of the siloles under the reaction conditions. Apparently this stability is rather
low for R = H, since in the reaction mixtures containing triethylborane 1 and Me₂Sn(C≡C-H)₂, a silole 3 could not be detected. In contrast, the corresponding stannole 3Sn can be isolated [8], since the 1,1-ethylboration of Me₂Sn(C≡C-H)₂ is already complete at –20 °C.

**Reaction of Diethynyl(dimethyl)silane 2 with triethylborane 1**

In the reaction of 2 with 1 at 80 °C, depending on reaction time, two major compounds were formed, and their NMR spectra could be analysed to propose a 7-silanorbornadiene derivative 4 and a 7-silanorbornene derivative 5 as the results of [4+2]cycloadDITIONS of 3 either with 2 or with a second molecule of 3, respectively (Scheme 2).

In the presence of a large excess of 2, the 7-silanorbornadiene 4 is the main product after 8 d at 80 °C. Isomers 4′ and 5′ (structures not assigned) are also formed. Their concentration (< 10%) was too low to allow for a complete assignment of all NMR data. Although alkynylsilanes are known to be weak dienophiles [9], the reactivity of the silole 3 is high enough to produce preferably the [4+2]cycloadDITION product 4 provided there is an excess of 2. If the concentration of 2 decreases, dimerisation of 3, in yet another [4+2]cycloadDITION, to 5 becomes competitive. This is graphically depicted in Fig. 1. The NMR data of the main products (Scheme 3) are in support of the proposed structures. Although, the NMR spectra indicate some decomposition, especially after 15 d at 80 °C, the steady increase in

Fig. 1. Changes in the concentration of 2, 4 and 5 as a function of reaction time at 80 °C, starting with a 3:1 molar ratio of Et₃B (1) / Me₂Sn(C≡C-H)₂ (2). The data are derived from ²⁹Si NMR spectra recorded by ¹H decoupled INEPT (refocused) experiments. The errors in these experiments with respect to quantitative analysis are believed to be similar for the compounds 2, 4 and 5. The addition of the concentrations in % does not sum up to 100%, since the intensities of signals of the minor isomers (< 5%) and of decomposition products are not included.

the concentration of 5 points towards a retro-Diels-Alder reaction of 4 and a dimerisation of 3 to 5. It appears that in the course of the dimerisation the boryl-substituted double bond in 3 is much more reactive than the other one. This is in agreement with the behaviour of alkynylboranes and alkenes as dienophiles in Diels-Alder reactions [10]. The endo-isomer is usually preferred [11], and the diethylboryl groups in 5 prefer positions distant to each other.

As is evident from Scheme 3 and Fig. 1, ²⁹Si NMR spectra are particularly instructive for monitoring the reaction between 1 and 2, and also for the determination of the product distribution. ¹¹B NMR spectra can be readily obtained from the reaction mixtures; however their diagnostic value is low, since only a single broad signal (δ¹¹B 87 ± 2) underneath the fairly sharp ¹¹B NMR signal for Et₃B can be observed. When 2 starts to react with 1, the ²⁹Si NMR signal for 2 (δ²⁹Si –38.9) becomes weaker and at first two other ²⁹Si NMR signals start to grow, at δ²⁹Si –26.1 and +82.7. The former signal is in the range expected for alkynyl(alkynyl)dimethylsilanes [12], whereas the latter one is typical of the 7-silanorbornadiene structure, where the ²⁹Si nucleus becomes extremely deshielded [13] when compared with other tetraorganosilanes. This deshielding is related to
the unique electronic structure of 7-silanorborendienes [14]. After several days, an increasing amount of the 7-silanorborene derivative 5 is formed, giving rise to two new $^{29}$Si NMR signals, one at $\delta^{29}$Si 42.5 (Si-7) and the other one at $\delta^{29}$Si 25.1 in the typical range for sila-2-cyclopentenes with two methyl groups attached to silicon [15].

Reactions of 1-alkynyl(ethylidimethyl)silanes 6 with triethylborane 1

Since the intermediary of the silole 3 could only be assumed, the reactions of 1 with 1-alkynyl-(ethylidimethyl)silanes, Me$_2$Si(C≡C-H)C≡C-R 6, were also studied. These reactions afford complex mixtures if R = Bu (6a) or $^3$Pent (6b), since two siloles 7a,b and 7’a,b (molar ratio ca. 3:2) are formed first (Scheme 4). Then, $[4+2]$cycloadditions of the siloles with the alkyenes 6a and 6b, respectively, lead to 7-silanorborendienes. This becomes evident from the $^{29}$Si NMR spectra which show the signals for the siloles 7 and 7’ (see Scheme 4) and 7-silanorborendienes [ $\delta^{29}$Si -27.9, +77.2; -28.8, +72.6 (R = Bu), and -27.8, +80.3, -28.8, +77.1 (R = $^3$Pent)]. Therefore, the proposed mechanism for the reaction of 2 with 1 is confirmed. The silole 3 must be the important intermediate. After more than 8 d of heating at 100 °C, numerous signals appear, some of which may be assigned to dimerisation products similar to 5 [e.g., $\delta^{29}$Si(7) +38.4, +44.0 (R = Bu), and +38.5, +44.1 (R = $^3$Pent)]. In the case of 6c (R = $^3$Bu), the formation of the silole 7c is preferred, since the Si-C≡C-$^3$Bu unit is much less reactive than the Si-C≡C-H unit, and according to the $^{29}$Si NMR spectra only a small amount of a 7-silanorborendiene (< 20%) ($\delta^{29}$Si -27.4, +71.1) is present in the reaction solution after 8 d at 100 °C. Clearly, the steric demand of a $^3$Bu group in 2-position at the silole ring does not favour further $[4+2]$-cycloadditions.

Conclusions

The results from this study indicate that siloles obtained from 1,1-organoborations of di(1-alkynyl)dimethylsilanes are reasonably stable under the reaction conditions (ca. 100 °C for several days), provided there are two organyl groups in 2,5-positions [1a]. If only one of the organyl groups is replaced by hydrogen as in 7 or 7’, the siloles are present in the reaction solutions, but they undergo $[4+2]$cycloadditions with the respective alkynylsilane, or they dimerise slowly in the absence of alkylene. If there are hydrogen atoms in 2,5-positions, the corresponding silole 3 cannot be detected under the reaction conditions (80 °C), and a 7-silanorborendiene- 4 and / or a 7-silanorborene derivative 5 are the major products.

Experimental Section

All preparative work and handling of the compounds was carried out in an inert atmosphere of nitrogen or...
argon. Solvents were carefully dried and glassware was used oven-dried. Triethylborane (Schering) was used as a commercial product, and the silanes 3 [16] and 6 [2a, 16] were prepared following the literature procedures. NMR measurements: Bruker AC 300 and Bruker ARX 250 [1H, 11B, 13C NMR, and 29Si NMR (refocused INEPT [17])]. Chemical shifts are given with respect to Me3Si [δ1H (CD3)2]H] 7.15; δ1H (CD3)2CD2H] 2.03; δ13C (CD3) 128.0; δ13C (CD3)2 CD3] 20.4; δ29Si = 0 for δ29Si = 19.867184 MHz], BF3·Et2O \[ δ11B = 0; δ29Si = 32.083971 MHz.

1,1-Ethylolation of the alkynylsilanes 3 and 6 (general procedure): Mixtures of triethylborane 1 and the respective alkynylsilane 3 or 6 (scale: 5 to 10 mmol; molar ratio ca. 3:1) were prepared at room temperature without a solvent, and heated at 80 °C (3, if the temperature is raised to 100 °C, decomposition becomes dominant) or 100 °C (6; the rate of the reaction is very slow at 80 °C) for several days (see e.g. Fig. 1). The same mixtures were also sealed in NMR tubes, together with a small amount of [D6]toluene, kept under the same conditions, and the progress of the reactions was monitored by 29Si NMR spectroscopy. A mixture containing 1 and 2 in a 1:8 molar ratio, heated at 80 °C for 6 d, was analysed by 29Si NMR to contain mainly (90%) the excess of 2 and the 7-silanobornadiene 4. After removing all volatile material in vacuo (1 and 2), colourless or yellowish oils were left and analysed by NMR. The same compounds (in the same ratio) were present as in the reaction solutions. Attempts to separate 4 by fractional distillation under reduced pressure led to decomposition. Decomposition of the reaction mixtures containing 1, 2, 4 and 5 or 1, 6, 7, 8 and [4+2]cycloaddition products was also observed by chromatography on silica or Al2O3 (elution with hexane gave only 2). 4: 1H NMR (500.13 MHz, CD2D6): δ = 0.04, 0.05, 0.24, 0.26 (4x, 12H, SiMe1, 1.15, 1.00 (m, t, 10H, BEt2), 2.40, 0.95 (m, t, 5H, 6-Et), 2.10 (s, 1H, =CH), 3.06 (broad, s, 1-1H), 6.88 (m, 1H, C=3-H), 3.07 (dd, J(H,H) 1.5 and 2.7 Hz, 1H, C=4-H), 7c: 13C [1H] NMR (75.5 MHz, CD2D6): δ = 131.9 (C=2), 162.2 (broad) (C=3), 146.3 (C=4), 119.5 (C=5), 32.8, 31.3 (2-1Bu), 20.0 (broad), 9.9 (BEt2), 28.5, 12.3 (4-Et), –1.7 (SiMe2).

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