Synthesis of 1,2-Dihydro-1,2,5-disilaborepines and 1,2-Dihydro-1,2-disilafulvenes *via* Organoboration and Hydroboration/Organoboration of 1,2-Diethynyltetramethyldisilane

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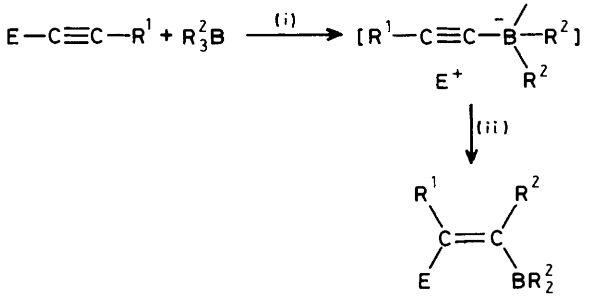
1,2-Diethynyltetramethyldisilane (**1**) reacts with trimethylborane (**2a**) or triethylborane (**2b**) to give the new 1,2-dihydro-1,2,5-disilaborepines (**3**) in good yield; in contrast a 1,2-dihydro-1,2-disilafulvene derivative (**5**) is the product of the reaction between (**1**) and tri-isopropylborane (**2c**), formed by an unprecedented sequence of hydroboration and intramolecular organoboration.

The organoboration of alkynylstannanes has opened the way to numerous new heterocyclic compounds.[1] The extension of this work to alkynylsilanes seemed an attractive target. However, it turned out that representative alkynylsilanes like $Me_3Si-C\equiv C-H$, $Me_2Si(C\equiv C-H)_2$, or $Me_3Si-C\equiv C-SiMe_3$ do not react with an excess of triethylborane, even when the mixtures are heated to *ca.* 100 °C for a prolonged time (7 days). Since the mechanism of the 1,1-organoboration requires the cleavage of the $Si-C\equiv$ bond in the first step of the reaction (*cf.* Scheme 1), this failure may be ascribed to the insufficient polarity of the $Si-C\equiv$ bond as compared to the $Sn-C\equiv$ bond in alkynylstannanes. Interestingly, 1,1-organoboration[2] and also 1,1-diboration[3] of alkynylsilanes has been reported using organoboron halides and 1,2-di-t-butyl-1,2-dichloro-diboronane(4), respectively. Obviously, an increase in the Lewis-acidity of the borane facilitates the cleavage of the $Si-C\equiv$ bond. Since the nature of the $Si-C\equiv$ bond may be of great importance, alkynyldisilanes are of interest owing to the predictable—albeit slight—increase in the polarity of their $Si-C\equiv$ bond as compared with that in alkynylmonosilanes. Therefore, it was decided to study the behaviour of 1,2-diethynyltetramethyldisilane (**1**) towards trialkylboranes (**2**).

As shown in Scheme 2, trimethylborane (**2a**) and triethylborane (**2b**) react with (**1**) to give the 1,2-dihydro-1,2,5-disilaborepines (**3a**) and (**3b**), respectively. The new heterocycles are obtained in pure state† by fractional distillation as colourless, air- and moisture-sensitive liquids. Although the reaction conditions are somewhat severe (see Scheme 2), there is only a little decomposition. In typical reactions [10 mmol of (**1**) and *ca.* 50 mmol of (**2**)] approximately 50% conversion of (**1**) into (**3**) can be achieved and the starting materials (**1**) and (**2**) are readily recovered and can be used again. In the case of the reaction between (**1**) and (**2b**), n.m.r. spectra of the reaction solution show weak ^{1}H, ^{13}C, and ^{29}Si resonances indicating the presence of the intermediate (**4b**).

The ^{1}H, ^{11}B, ^{13}C, and ^{29}Si n.m.r. data of the new heterocycles (**3**) are given in Table 1. In addition to routine techniques for assigning ^{13}C resonances, the observation of the broad ^{13}C resonances for boron-bonded carbon atoms[4,5]



Scheme 1. (i) For various stannyl groups (E) and bulky groups R^1 the existence of the borate-like intermediate is supported by n.m.r. spectroscopic evidence (^{11}B, ^{119}Sn n.m.r.).[1] (ii) For various stannyl groups (E) this stereochemistry has been found in most cases studied.[1]

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† (**3a**): B.p. 38—40 °C/200 Pa. (**3b**): b.p. 51—53 °C/60 Pa. Elemental analyses and molecular weights (m.s.) are in agreement with the structures shown; n.m.r. data: see Table 1.

Table 1. ^1H, ^{11}B, ^{13}C, and ^{29}Si n.m.r. data[a,b] of the 1,2-dihydro-1,2,5-disilaborepines (**3**).

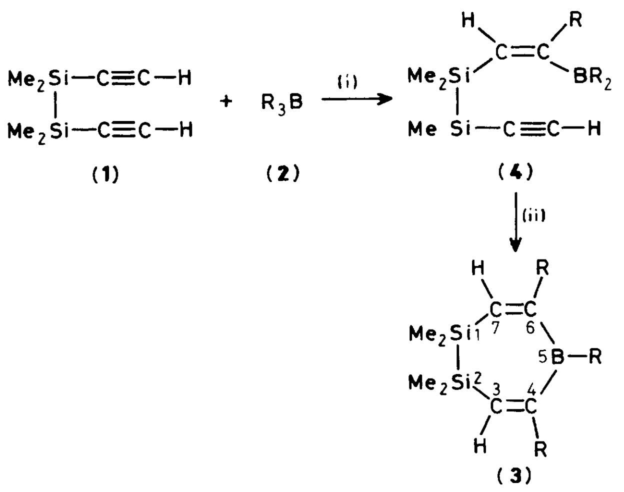
		$\delta^{13}C$ (δ^1H)								$\delta^{11}B$	$\delta^{29}Si$
	R	C(1′,2′)		C(3,7)		C(4–4″,6–6″)		C(5′,5″)			
(**3a**)	Me	−2.0	(0.15)	131.5	(5.93)	166.8	(−)	13.8	(0.89)	80.3	−29.9[d]
		[43.9]	s, 12H	[58.6]	q,[c] 2H	[br]		[br]	s, 3H		
		{120.2}		{134.7}		26.1	(1.85)				
						{126.0}	d,[e] 6H				
(**3b**)	Et	−1.8	(0.10)	126.4	(5.81)	173.0	(−)	22.7	(1.38)	81.8	−30.3
		[45.0]	s, 12H	[59.8]	t,[f] 2H	[br]		[br]	q, 2H		
		{119.9}		{133.8}		30.7	(2.19)	8.5	(0.97)		
							d, q, 4H		t, 3H		
						12.9	(1.02)				
							t, 6H				

[a] Bruker WP 200, Bruker AC 300; (**3a**) in C_7D_8, (**3b**) in $CDCl_3$; solutions *ca.* 10% v/v; at 27—28 °C in 5 mm (o.d.) tubes. [b] Chemical shifts, references: ^1H (Me_4Si, internal), given in parentheses after the $\delta^{13}C$ values, multiplicity and relative number of protons given below; ^{11}B (BF_3–OEt_2, external); ^{13}C [Me_4Si, $\delta^{13}C$(solvent) 20.4 ($C_6D_5CD_3$), 77.0 ($CDCl_3$)]; ^{29}Si (Me_4Si, external). Coupling constants $^1J(^{29}Si^{13}C)$ (± 0.6 Hz) are given in square brackets and $^1J(^{13}C^1H)$ (±0.2 Hz, from ^1H n.m.r.) in { }; [br] denotes the broad resonances relaxation of the second kind) of boron-bonded ^{13}C nuclei.[4,5] [c] $^4J(^1H^1H)$ 1.8 Hz. [d] $^2J(^{29}Si^1H)$ 5.2 Hz. [e] $^4J(^1H^1H)$ 1.5 Hz.

and of ^{29}Si satellites [*e.g.*, $^1J(^{29}Si^{13}C$-3/7)] strongly supports the structure (**3**). The ^{11}B nuclear shielding in (**3**) ($\delta^{11}B$ *ca.* 80) is reduced with respect to various boracyclohexadienes (range of $\delta^{11}B$: 55 to 72[4,5b]) containing the analogous structural unit as far as the boron atom is concerned, but it is similar to that for the derivatives of (**3**) with trimethylstannyl groups in the 3- and 7-positions.[6]

The presence of the intermediate (**4b**) is inferred from two ^{29}Si resonances fitting exactly the Si–C≡ ($\delta^{29}Si$ −35.8) and the SiC= environment ($\delta^{29}Si$ −27.8) and also from all the complementary ^1H,^{13}C n.m.r. data. Therefore, it is concluded that the organoboration of (**1**) proceeds stepwise (Scheme 2) according to the mechanism outlined in Scheme 1.

Tri-isopropylborane (**2c**) does not react with (**1**) below 100 °C, either in toluene or without a solvent. When heated to 120 °C for 48 h without a solvent, a small fraction of a volatile compound (**5**)‡ could be separated by distillation, leaving the bulk of the reaction products as a brown, polymeric residue. If the same reaction was carried out in toluene as a solvent (115 °C/48 h), a small amount of a mixture of the compounds (**5**) and (**6**) was obtained by distillation (Scheme 3). The formation of compound (**5**) is initiated by thermally induced dehydroboration[7] of tri-isopropylborane (**2c**) leading to Pr^i_2BH and propene. After this, one of the further reaction pathways may involve the hydroboration of (**1**) by Pr^i_2BH to give the intermediate (**7**) (weak ^1H, ^{13}C, and ^{29}Si resonances in the n.m.r. spectra of the reaction solution) which is then converted by intramolecular organoboration into (**5**). This assumption has been confirmed experimentally using an equilibrated mixture of (**2c**) and BH_3–THF in THF)[8] [tenfold excess of (**2c**)] for the reaction with (**1**) instead of pure (**2c**). By this route the yield [based on (**1**)] for compound (**5**) was improved from *ca.* 5% to *ca.* 30%. The existence of the Pr^i(Pr)B-group in compound (**6**) can be explained taking into account a sequence of dehydroboration/hydroboration (of propene)/dehydroboration for (**2c**), leading to Pr^i(Pr)BH as the reactive boronhydride.



Scheme 2. (i) (**2a**; R = Me), (**2b**; R = Et); reaction conditions: (**1**) + (**2a**) 3 days at 120—130 °C in toluene in a sealed tube under Me_3B-pressure (*ca.* fivefold excess of Me_3B); (**1**) + (**2b**) 7 days at 115 °C in refluxing toluene (*ca.* fivefold excess of Et_3B). (ii) Only (**4b**) has been detected by n.m.r. in the reaction solution.

The structures of (**5**) and (**6**) follow conclusively from the n.m.r. data.‡ The assignment of the ^{29}Si resonances is based on selective ^1H spin population transfer experiments[9] and the ^1H resonances were assigned by n.O.e. difference spectroscopy.[10]

Hydroboration of alkynylsilanes has received only scant attention so far. The determination of the stereochemistry proved that the boron atom attacks preferentially at the site of the Si–C≡ carbon atom in the absence of serious steric

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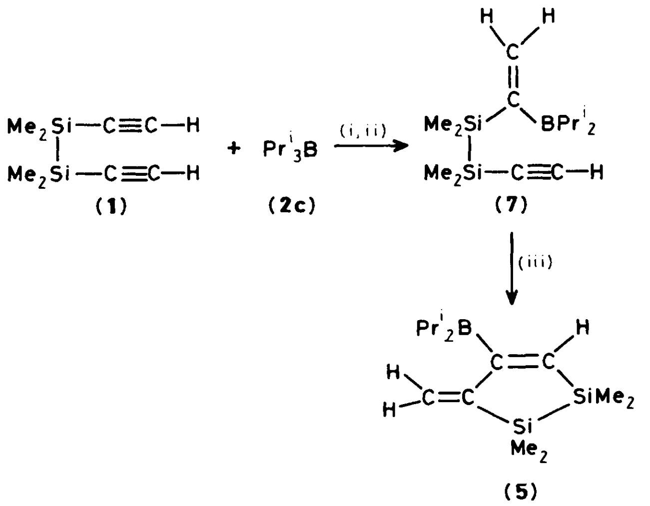
‡ (**5**): B.p. 40—45 °C/133 Pa. N.m.r. in $CDCl_3$; ^1H n.m.r.: δ^1H = 0.15 s, 6H Si*Me*$_2$; 0.17 s, 6H, Si*Me*$_2$; 0.92 d, 12H, $B[CH(CH_3)_2]_2$; 1.51 sept., 2H, $B[CH(CH_3)_2]_2$; 5.23 d, 1H, $C=CH_2$; 5.27 dd, 1H, $C=CH_2$; 5.62 d, 1H, SiC*H*=. ^{13}C n.m.r.: $\delta^{13}C[^1J(^{29}Si^{13}C)]$ = −4.4 Si*Me*$_2$; −3.4 Si*Me*$_2$; 24.4, 18.2, BPr^i_2; 123.5 = CH_2; 134.0[58.8] Si*C*H=; 159.0 [59.5] Si*C* = CH_2; 177.0 B*C* =. ^{29}Si n.m.r.: $\delta^{29}Si$ = −22.8 *Si*–CH=; −17.2 *Si*–C=CH_2. Mixture of (**5**) and (**6**) (*ca.* 1 : 1): b.p. 40—45 °C/133 Pa. (**6**):^{29}Si n.m.r.: $\delta^{29}Si$ = −22.4 *Si*–CH=; −17.1 *Si*–C=CH_2.



Scheme 3. (i) Without solvent 48 h at 120 °C [*ca.* fivefold excess of (**2c**)]; compound (**5**) (*ca.* 85% pure) was obtained in *ca.* 5% yield; in toluene 48 h at 115 °C [*ca.* fivefold excess of (**2c**)] a mixture of (**5**) and (**6**) (*ca.* 1 : 1) together with some minor impurities (<10%) was obtained in *ca.* 5% yield; (**6**) has the same structure as (**5**) but the Pr^i_2B group is replaced by the $Pr^i(Pr)B$ group.‡ (ii) A mixture of (**2c**) and BH_3–THF [1.5 M in THF, *ca.* tenfold excess of (**2c**)] was stirred at 25 °C for 24 h, cooled to 0 °C and a solution of (**1**) [ratio of (**1**) to BH_3: 1/3] in THF was added; after warming to room temperature the THF was distilled off at normal pressure and the fractional distillation of the residue gave pure (**5**) (b.p. 43—45 °C/133 Pa) in 30% yield. (iii) Several weak signals indicate the presence of the intermediate (**7**) when the reaction is monitored by n.m.r. (weak ^{29}Si resonances: $\delta^{29}Si = -36.2$ *Si*–C≡, −24.2 *Si*–C=).

hindrance.[11,12] The present results show clearly that there is considerable synthetic potential in combining stereoselective hydroboration reactions with intramolecular organoboration.

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