Synthesis, catalytic condensation, and silylation of 1,2-dihydrobenzo-1,3,2-diazaboroles

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Catalytic condensation of phenyl- and benzyl-1,2-dihydrobenzo-1,3,2-diazaboroles in the presense of catalysts occurs without cleavage of the B—N bond and yields polycyclic compound **2**. Treatment of dihydrobenzodiazaboroles with methylphenylsilane gives B, Si, N-containing compounds.

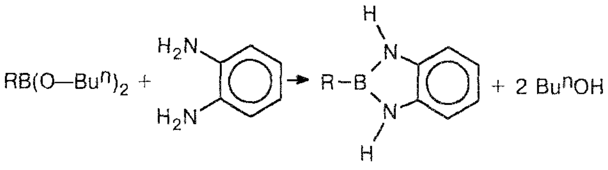
Key words: dihydrobenzodiazaboroles, catalytic condensation, silylation, polycyclic boron-nitrogen compounds.

Polycyclic boron-nitrogen-containing compounds, particularly, polyorganocycloborazines possess high thermal and hydrolytic stability.

The purpose of the present work is to establish whether it is possible to use catalytic polycondensation for synthesizing polycyclic boron-nitrogen-containing compounds and mixed boron-nitrogen-silicon-containing compounds.

Dihydrobenzodiazaboroles **1a—c** synthesized from esters of organylboric acids and *o*-phenylenediamine using a method analogous to one described previously[1] were used as the starting boron-containing heterocycles.

Scheme 1



1a—c

R = Ph (**a**), R = Tol (**b**), Bu^n (**c**)

The yields and properties of the resulting compounds **1a—c** are presented in Table 1. The condensation of **1a—c** was carried out at 280 °C in a dry inert atmosphere in the presence of catalysts, namely, KOH and metallic potassium (Table 2). The catalytic action of alkaline metals in reactions involving organosilazanes is based on one-electron reduction of the starting heterocycles to radical anions, which subsequently decompose to give an anion and the corresponding radical. This initiates radical substitution of organosilazanyl groups for the organic groups at the Si atoms.[2]

Table 1. Properties of compounds **1a—c**

Compound	Yield (%)	M.p. /°C	Molecular formula	Found/Calculated (%) C	H	N	B
1a	65	209	$C_{12}H_{11}BN_2$	74.2 74.2	5.7 5.7	14.2 14.4	5.6 5.7
1в	40	80	$C_{14}H_{15}BN_2$	73.8 75.0	6.4 6.8	12.8 12.6	5.0 4.9
1c	67	79	$C_{10}H_{15}BN_2$	64.5 69.0	8.2 8.7	16.3 16.1	5.4 6.2

Table 2. Thermal condensation of dihydrobenzodiazaboroles **1a—c**

Compound	Catalyst (mass %)	Reaction time /h	*T* /°C	Reaction products liquid (mol/mol)	Reaction products solid
1a	KOH, 2	2	218—290	C_6H_6, 3 : 4	**2**
1в	K, 1	1.12	110—220	C_7H_8, 1 : 2	**2**
1c	K, 1	4	110—280	—	*
1c+5 % **1a**	K, 1.2	4	110—290	—	**

* 83 % compound **1c** was isolated. ** 71 % compound **1c** and 5 % compound **2** were isolated.

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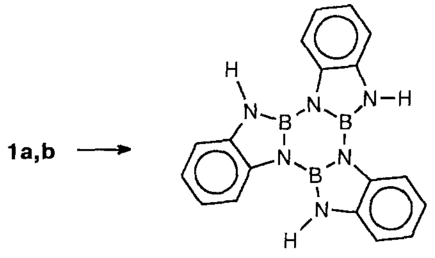
The condensation of compounds **1a** and **1b** is accompanied by liberation of benzene and toluene, respectively, and gives polycyclic compound **2**, which has been obtained previously[3] from tributyl borate and *o*-phenylenediamine.

Scheme 2



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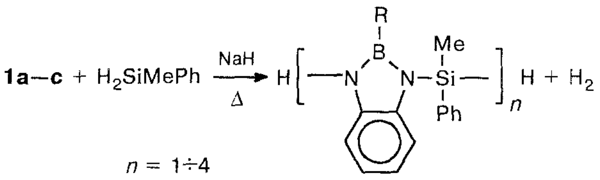
Probably, the high yield (80 %) of compound **2**, which contains dihydrobenzodiazaborole fragments and a borazine ring, originates from the stability of the B—N bond and the tendency of boron-nitrogen-containing compounds to form rings. It is interesting to compare the behavior of compounds **1a—c** with that of organocyclosilazanes. The thermal condensation of trimethyltriphenylcyclotrisilazane in the presence of KOH is accompanied by intense liberation of benzene, ammonia, and a small amount of hydrogen[4] at 200 °C, *i.e.*, this reaction involves decomposition of cyclotrisilazanes and the formation of compounds containing new linear and cyclic moieties. In addition, the following reactions accompany the replacement of the hydrocarbon groups at the Si atom: heterolytic condensation involving the amino groups, opening of the silazane rings at the Si—N bond, anionic rearrangements of the silazane rings,[2] *etc.*

Unlike compounds **1a** and **1b**, dihydrobenzodiazaborole **1c** underwent almost no transformations when heated for 4 h at 200—280 °C (~80 % of the original compound was recovered). An attempt to initiate thermal condensation of compound **1c** by adding 5 % compound **1a** failed. The transformation of compound **1a** into **2** did not cause changes in **1c**.

We considered the possibility of synthesizing Si,B,N-containing compounds from **1a** and various halosilanes. However, treatment of **1a** with trimethylchlorosilane or trimethyliodosilane in the presence of triethylamine or pyridine, as well as treatment of a Li-derivative of **1a** with trimethylchlorosilane, did not afford silylated derivatives of **1a** (up to 70 % of the original compounds was recovered even after prolonged action of the silylating agents).

We also studied the dehydrocondensation of compounds **1a—c** with methylphenylsilane in the presence of NaH (1 %):



The amount of hydrogen evolved in this reaction depends on the reaction time and the nature of the starting compound **1** (Table 3). In the case of compounds **1a** and **1b**, benzene or toluene were formed along with polycyclic compound **2** (3 % and 30 %, respectively). The reactions resulted mainly in mixtures of oligomeric compounds that were difficult to separate. The IR spectra of these mixtures contain an absorption band in the 895 cm^{-1} region, which indicates the presence of the Si—N bond. The data of elemental analysis (see Table 3) for a product obtained from compound **1b** are in agreement with structure **3**.

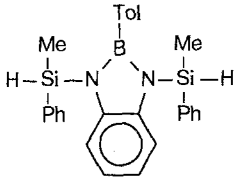


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Table 3. Dehydrocondensation of dihydrobenzodiazaboroles **1a—c**

Reagents	Time /h	Reaction temperature /°C	Gaseous products mol/mol	Yield of the end products (%)	M.p. /°C	Found/Calculated (%) C	H	B	N	Si
1a+MePhSiH$_2$	3	126—280	1 : 1	78	84—112	71.58 72.56	5.73 6.05	3.50 3.53	8.59 8.91	9.43 8.94
1b+MePhSiH$_2$	2	130—220	1 : 1	57	—	65.61 70.74	6.09 6.89	2.15 2.54	7.39 6.60	11.85* 13.23
1c+MePhSiH$_2$	2.3	110—224	1 : 1	81	50—54	—	—	—	—	—
1c+MePhSiH$_2$	6	110—200	1 : 2	84	—	68.85 69.87	7.59 7.24	3.72 3.72	9.85 9.85	—**

* Elemental analysis was carried out for compound **3**. ** M$_n$ of reaction products: 640.

Experimental

The compounds obtained were analyzed on a LKhM-8MD gas-liquid chromatograph (300 cm columns with 5 % SE-30 on Chromaton N-AW-HMDS). The melting points were determined by the capillary method. The molecular weights were found by ebulioscopy in benzene. IR spectra were recorded on a UR-20 spectrophotometer.

$RB(OBu^n)_2$ and Me_3SiI were synthesized according to procedures reported previously.[5,6]

General procedure for the preparation of 2-R-1,2-dihydrobenzo-1,3,2-diazaboroles (1a—c). A mixture of $RB(OBu^n)_2$ (0.1 mol) and *o*-phenylenediamine (0.1 mol) was heated at 120—130 °C; BuOH was distilled off during the reaction. The residue was recrystallized from benzene. (Compound **1c** was purified by sublimation at 120—140 °C (1—2 Torr)). The characteristics of the compounds are given in Table 1.

General procedure for the condensation of 1a—c. The B,N-heterocycles **1a—c** were heated with a catalyst; the gases and the liquid that evolved were collected (see Table 2). Polycyclic compound **2** was dissolved in acetone and precipitated with pentane.

Treatment of compound 1a with Me_3SiI. Me_3SiI (0.02 mol) was added dropwise over a period of 15 min to a mixture of compound **1a** (0.02 mol) and triethylamine (0.045 mol). The reaction mixture was stirred for 0.5 h at 40 °C, dry benzene (50 mL) was added, and the mixture was stirred for an additional 3 h. Work-up of the solution in benzene gave the original **1a** and Me_3SiI in 67 and 74 % yields, respectively.

Treatment of compound 1a with BuLi and Me_3SiCl. A solution of BuLi (43 mL, 0.78 *N*) was added at 30—40 °C over a period of 1 h under argon to a suspension of compound **1a** (0.17 mol) in heptane (50 mL), then the mixture was stirred for 5 h at the same temperature (after the reaction, the reaction mixture had pH 7). A solution of Me_3SiCl (0.034 mol) in heptane (20 mL) was added over a period of 0.5 h to the reagent obtained, and the mixture was stirred for 6 h at 40 °C. The mixture was decanted, and distillation of the solution gave Me_3SiCl (68 %). The precipitate was worked-up with 100 mL of a water—acetone mixture (30 : 70), filtered, and concentrated. The residue was recrystallized from benzene to give 63 % of compound **1a**.

General procedure for dehydrocondensation. A mixture of equimolar amounts of compounds **1a—c** with $MePhSiH_2$ was heated in the presence of NaH (1 mass %) (see Table 3). The reaction temperature was gradually increased and the gas that evolved was collected until the formation of low-molecular products ceased. The glassy precipitate was dissolved in benzene, the catalyst was filtered off, and the benzene was removed *in vacuo*. The characteristics of the products obtained are presented in Table 3.

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