# PREPARATION OF ORGANOSILICON-SUBSTITUTED **BORAZENES\***

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Abstract—The preparation of four B-tris-(triorganosilylmethyl)-N-trimethylborazenes by the Grignard method, of B-tris-(trimethylsiloxy)-N-trimethylborazene using sodium trimethylsilanolate and of B-tris-(triphenylsilyl)-N-trimethylborazene by means of triphenylsilyllithium is described.

The compounds in which the boron and silicon atoms are linked by a methylene group are stable toward hydrolysis, but those containing the B-O-Si and B-Si linkages are not. All are not oxidized by atmospheric oxygen under normal conditions.

OUR recent work<sup>(1)</sup> concerning the preparation and properties of organosilicon-substituted triorganoboranes has led to interest in organosilicon-substituted boron compounds which might be oxidatively stable. For this reason we have investigated the synthesis and properties of various types of organosilicon-substituted borazenes.

It has been shown recently<sup>(2-5)</sup> that B-trichloro-N-triorganoborazenes could be alkylated or arylated using the Grignard method. We have used this procedure to prepare several B-tris-(trisorganosilylmethyl)-N-trimethylborazenes (Ia-c), as well as B-tris-(pentamethyldisiloxanylmethyl)-N-trimethylborazene (Id), in good yields. These compounds were stable toward air oxidation and toward hydrolysis under neutral or mildly alkaline conditions. B-tris-(trimethylsilylmethyl)-N-trimethylborazene was not decomposed by alkaline hydrogen peroxide at room temperature. On the other hand, B-tris-(trimethylsiloxy)-N-trimethylborazene (II), prepared by the reaction of sodium trimethylsilanolate with B-trichloro-N-trimethylborazene, was not hydrolytically stable.

The reaction of triphenylsilyllithium with B-trichloro-N-trimethylborazene resulted in the first reported compound containing a boron-silicon bond, B-tris-(triphenylsilyl)-N-trimethylborazene (III),† This crystalline borazene derivative was stable to dry air, but proved to be quite susceptible to hydrolysis, which caused not only Si-B rupture but also complete destruction of the borazene ring

 $[(C_6H_5)_3SiBNCH_3]_3 + 9H_2O \rightarrow 3(C_6H_5)_3SiH + 3B(OH)_3 + 3CH_3NH_2.$ 

It was of interest to compare the infra-red spectra of the compounds prepared in

- (2) S. J. GROSZOS and S. F. STAFIEJ, J. Amer. Chem. Soc. 80, 1357 (1958).
- (a) H. J. BECHER and S. FRICK, Z. Anorg. Chem. 295, 83 (1958).
   (a) G. E. RYSCHKEWITSCH, J. J. HARRIS and H. H. SISLER, J. Amer. Chem. Soc. 80, 4515 (1958).
- <sup>(5)</sup> L. F. HOHNSTEDT and D. T. HAWORTH, Abstracts of Papers presented at the 132nd Meeting of the American Chemical Society, New York, September, 1957, p. 8-S.

<sup>\*</sup> Presented at the Fifteenth Southwest Regional Meeting of the American Chemical Society, Baton Rouge, December, 1959.

<sup>†</sup> Note added in proof: After our paper was submitted, the communication of CowLey, SISLER and RYSCHKEWITSCH, J. Amer. Chem. Soc. 82, 501 (1960), appeared in which they described  $[(C_6H_5)_3SiBNMe]_3$ as a yellow highly viscous oil. However, their chemical and infra-red data agree with those reported in this paper for our compound of m.p. 248-251°. We can offer no explanation for this difference in physical properties at this time.

<sup>&</sup>lt;sup>(1)</sup> D. SEYFERTH, J. Amer. Chem. Soc. 81, 1844 (1959).



this study with those of other B-trisubstituted-N-trimethylborazenes. The effect of the substituents on the boron atom on the B-N bond is apparent from the shift of the intense band assigned by PRICE *et al.*<sup>(6)</sup> to in-plane vibrations of the borazene ring. Table 1 lists the frequencies given for this band in a number of compounds. The values listed are consistent with the effects on the strength of the B-N bond to be

Compound	Borazene ring frequency (cm <sup>-1</sup> )	Ref.
(CH <sub>3</sub> NBCl) <sub>3</sub>	1458	7
(CH <sub>3</sub> NBOCH <sub>3</sub> ) <sub>3</sub>	1449	7
(CH <sub>3</sub> NBH) <sub>3</sub>	1425	6
(CH <sub>3</sub> NBOC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	1412	7
(CH <sub>3</sub> NBOSiMe <sub>3</sub> ) <sub>3</sub>	1407	this work
(CH <sub>3</sub> NBC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	1405	3
(CH <sub>3</sub> NBC <sub>2</sub> H <sub>6</sub> ) <sub>8</sub>	1404	4
(CH <sub>3</sub> NBC <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	1401	4
(CH <sub>3</sub> NBCH <sub>2</sub> CHC=H <sub>2</sub> ) <sub>3</sub>	1401	4
(CH <sub>3</sub> NBCH <sub>2</sub> SiMe <sub>3</sub> ) <sub>3</sub>	1387	this work
(CH <sub>3</sub> NBCH <sub>2</sub> SiMe <sub>3</sub> OSiMe <sub>3</sub> ) <sub>3</sub>	1384	this work
[CH <sub>3</sub> NBSi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub>	1339	this work

 TABLE 1.—FREQUENCIES DUE TO IN-PLANE VIBRATIONS OF THE BORAZENE RING

 IN SOME B-TRI-SUBSTITUTED-N-TRIMETHYLBORAZENES

<sup>(8)</sup> W. C. PRICE, R. D. B. FRASER, T. S. ROBINSON and H. C. LONGUET-HIGGINS, Disc. Faraday Soc. 9, (131) (1950).

<sup>(7)</sup> M. J. BRADLEY, G. E. RYSCHKEWITSCH and H. H. SISLER, J. Amer. Chem. Soc. 81, 2635 (1959).

expected for the various substituents on the boron atoms. Thus electron-attracting substituents, such as alkoxy, trimethylsiloxy, phenoxy and phenyl groups, cause a shift to higher frequencies relative to unsubstituted normal alkyl groups, i.e., a strengthening of the B-N bond by withdrawal of electron-density from boron. On the other hand, electron-releasing groups, such as trimethylsilylmethyl and pentamethyldisiloxanylmethyl, cause a shift to lower frequencies, which may be interpreted as a weakening of the B-N bond due to the positive inductive effect of these groups which opposes back donation from nitrogen to boron.

# **EXPERIMENTAL\***

#### 1. Starting Materials

The method of BROWN and LAUBENGAYER<sup>(8)</sup> was used to prepare the quantities of (MeNBCl)<sub>3</sub> required. Trimethylchloromethylsilane,<sup>(9)</sup> ethyldimethylchloromethylsilane,<sup>(10)</sup> and pentamethylchloromethyldisiloxane<sup>(11)</sup> are all known compounds and were prepared by established methods. n-Butyldimethylchloromethylsilane, a new compound, was prepared by the reaction of 3.6 moles of  $n-C_4H_0MgBr$  with 3 moles of Me<sub>2</sub>(CH<sub>2</sub>Cl)SiCl in diethyl ether solution in 34 per cent yield.

 $n-C_4H_9(CH_3)_2SiCH_2Cl, b.p. 77-78^{\circ}/29 \text{ mm}, n_p^{25}$  1.4331. (Found: C, 50.31; H, 10.64. Calc. for C<sub>7</sub>H<sub>17</sub>ClSi: C, 51.03; H, 10.4%)

Sodium trimethylsilanolate was prepared by the reaction of sodamide with hexamethyldisiloxane in liquid ammonia solution.(12)

## 2. B-tris-(Trimethylsilylmethyl)-N-Trimethylborazene (Ia)

A suspension of 30 g (0.13 mole) of (MeNBCl)<sub>3</sub> in 400 ml of anhydrous diethyl ether was prepared in a 21. three-necked flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel. To this was then added with vigorous stirring during the course of 1 hr the Grignard reagent prepared from 73.5 g (0.6 mole) of Me<sub>3</sub>SiCH<sub>2</sub>Cl and 14.5 g (0.6 g atom) of magnesium turnings in 350 ml of ether. A white precipitate of MgCl<sub>2</sub> formed immediately. The mixture was heated at reflux for 6 hr and left to stand overnight at room temperature. The flask was cooled to 0° and the reaction mixture was hydrolysed with saturated ammonium chloride solution. The organic layer was decanted and the residual salts were washed with three 75 ml portions of ether. The combined organic layer and ether washings were washed with four 100 ml portions of distilled water and subsequently were dried over anhydrous sodium sulphate. Filtration was followed by removal of the ether at reduced pressure. Forty-four grammes of an oily solid remained. To this was added a small quantity of methanol; filtration gave 17 g of white crystalline solid. The filtrate was distilled. The fraction distilling between  $110-170^{\circ}$  at 0.8 mm crystallized in part in the receiver. The crystals were freed from oil by washing with methanol as before. Further solid was obtained by chilling the methanol washings. In this manner a total of 29 g (58.5 per cent) of compound Ia resulted. An analytically pure sample, m.p. 64°, was obtained by recrystallization from methanol. (Found: C, 47.02; H, 11.29; N, 11.13. B, 8.75; mol. wt. (Rast), 394. Calc. for  $C_{15}H_{42}N_3B_3Si_3$ : C, 47.25; H, 11.1; N, 11.02; B, 8.51%; mol. wt., 381·3).

During one such preparation a deficiency of Me<sub>3</sub>SiCH<sub>2</sub>MgCl was inadvertently used, and a small amount of a second substance crystallized from a higher boiling (155-210° at 0.7 mm) fraction on cooling. Recrystallization from methanol gave white crystals, m.p. 95-96°. These were tentatively

- (\*) F. C. WHITMORE and L. H. SOMMER, J. Amer. Chem. Soc. 68, 483 (1946).
   (10) A. D. PETROV, V. F. MIRONOV and N. A. POGONKINA, Dokl. Akad. Nauk SSSR 100, 81 (1955).

<sup>\*</sup> Analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Melting points are uncorrected and were determined on a Fisher-Johns block. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen.

<sup>(8)</sup> C. A. BROWN and A. W. LAUBENGAYER, J. Amer. Chem. Soc. 77, 3699 (1955).

<sup>(11)</sup> R. H. KRIEBLE and J. R. ELLIOTT, J. Amer. Chem. Soc. 67, 1810 (1945). (12) J. F. HYDE, O. K. JOHANNSON, W. H. DAUDT, R. F. FLEMING, H. B. LAUDENSLAGER and M. P. ROCHE, J. Amer. Chem. Soc. 75, 5616 (1953).

identified as N,N,N,N',N',N'-hexamethyl-B,B,B',B'-tetrakis-(trimethylsilylmethyl)-B,B'-bisborazene oxide. (Found: C, 44.08, 44.32; H, 10.30, 10.29; N, 14.00, 13.97; B, 11.03. Calc. for C<sub>12</sub>H<sub>62</sub>N<sub>6</sub>OB<sub>6</sub> Si<sub>4</sub>: C, 43.74; H, 10.34; N, 13.91; B, 10.75%.)



# Chemical properties of (MeNBCH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>

(a) Thermal stability. A small sample of compound Ia was placed in a small test tube and the tube was evacuated and sealed off. The tube was then heated at 380° for 30 min. This treatment caused no change in the melting point (64°) of the sample. Heating of the compound in an open test tube at 250° for 15 min caused a lowering of the m.p. to 57-58°. Similarly, distillation of a small sample at atmospheric pressure (bath temperature 250°) lowered the m.p. to 59-60°.

(b) Hydrolytic stability. A small sample (213 mg) of the compound was heated at 100° in 20 ml of water for 1 hr. A 98 per cent recovery (209 mg) of the sample was achieved. No change in m.p. was observed after this treatment. No amine odour was noticed when a small sample of compound Ia was refluxed in 2 N NaOH solution for 1 hr. A quantitative recovery of unchanged borazene (m.p. 64°) was obtained. However, no Ia could be recovered after it had been refluxed with 3 N HCl for 1 hr.

(c) Oxidation stability. Compound Ia was not affected by alkaline hydrogen peroxide and could be recovered unchanged after being kept at room temperature in this reagent overnight.

It may be noted that SISLER et  $al.^{(4)}$  found B-trialkyl-N-trimethylborazenes more resistant to hydrolysis and oxidation than borazene itself, reflux with hydrogen peroxide in 50 per cent sulphuric acid being required to effect complete degradation of their compounds.

#### 3. B-tris-(Ethyldimethylsilylmethyl)-N-Trimethylborazene (Ib)

A procedure similar to that described for compound Ia was used in the reaction of the Grignard reagent prepared from 109.4 g (0.8 mole) of Me\_EtSiCH\_2Cl and 0.8 g atom of magnesium with 0.15 mole of (MeNBCl)<sub>2</sub> in ether solution. Seventy grammes of a light yellow oil resulted which was distilled at reduced pressure. The fraction distilling at 160–185° at 1.0 mm was collected and redistilled to give 38 g (60 per cent) of pure compound Ib b.p. 183–184° at 1.0 mm,  $n_{25}^{55}$  1.4875,  $d_{4}^{44}$  0.8977. (Found: C, 51.18; H, 11.31; N, 10.31. Calc. for C<sub>18</sub>H<sub>48</sub>N<sub>2</sub>B<sub>3</sub>Si<sub>3</sub>: C, 51.05; H, 11.4; N, 9.93%.)

#### 4. B-tris-(n-Butyldimethylsilylmethyl)-N-trimethylborazene (Ic)

A similar procedure was used in the reaction of the Grignard reagent prepared from 132 g(0.8 mole) of n-BuMe<sub>3</sub>SiCH<sub>3</sub>Cl and 0.8 g atom of magnesium with 0.17 mole of (MeNBCl)<sub>2</sub>. After hydrolysis and distillation of the solvent, 110 g of a yellowish oil remained. Distillation at reduced pressure gave 59 g (69 per cent) of crude compound Ic, b.p. 208-217° at 0.8 mm. A second fractional distillation resulted in 43.7 g (57 per cent) of pure material, b.p. 213-214° at 0.9 mm,  $n_{D}^{26}$  1.4845,  $d_{4}^{45}$  0.8855. (Found: C, 56.70, 56.96; H, 11.87, 11.93; N 8.13, 8.17; B, 6.72, 6.60. Calc. for C<sub>24</sub>H<sub>60</sub>N<sub>3</sub>B<sub>3</sub>Si<sub>3</sub>. C, 56.79; H, 11.92; N, 8.28; B, 6.39%.)

#### 5. B-tris-(Pentamethyldisiloxanylmethyl)-N-Trimethylborazene (1d)

The reaction between 0.8 mole of  $Me_3SiOSiMe_2CH_3MgCl$  and 0.15 mole of (MeNBCl)<sub>3</sub> in ether solution was carried out using the procedure described above. Distillation of the liquid residue obtained after hydrolysis and distillation of the ether gave 55 g of a fraction distilling at 161–190° at 0.9 mm. A second distillation resulted in 45 g (50 per cent) of colourless compound Id, b.p. 175–176°

at 0.55 mm,  $n_{25}^{25}$  1.4517,  $d_{45}^{45}$  0.9158. (Found: C, 41.83%, H, 10.33; N, 7.11; B, 5.88. Calc. for  $C_{11}H_{40}O_{3}N_{3}B_{2}Si_{3}$ : C, 41.77; H, 10.02; N, 6.96; B, 5.37%.)

## 6. B-tris-(Trimethylsiloxy)-N-Trimethylborazene (II)

To a suspension of 37 g (0.165 mole) of (MeNBCl)<sub>s</sub> in 300 ml of ether under a nitrogen atmosphere was added during a period of 45 min with vigorous stirring a solution of 88.5 g (0.7 mole) of sodium trimethylsilanolate in 450 ml ether. A slightly exothermic reaction was observed and sodium chloride precipitated. The reaction mixture was refluxed for 6 hr, then was cooled and filtered. Evaporation of most of the ether from the filtrate caused precipitation of some of the excess Me<sub>3</sub>SiONa. Filtration was followed by addition of 24 g (0.22 mole) of Me<sub>3</sub>SiCl in 150 ml of ether to the filtrate in order to destroy any Me<sub>3</sub>SiONa still present by the reaction

$$Me_{a}SiONa + Me_{a}SiCl \rightarrow Me_{a}SiOSiMe_{a} + NaCl.$$

Filtration of the precipitated NaCl was followed by distillation of the filtrate. A 60 per cent yield  $(37 \cdot 5 \text{ g})$  of compound II, b.p. 129–131° at 0.85 mm, was thus obtained. An analytically pure sample could be gotten by a further fractional distillation (b.p. 130° at 0.85 mm, m.p. 22–23°). (Found: C, 37·37; H, 9·31; N, 11·27' B, 8·22. Calc. for C<sub>12</sub>H<sub>36</sub>O<sub>3</sub>N<sub>3</sub>B<sub>3</sub>Si<sub>3</sub>: C, 37·23; H, 9·37; N, 10·85; B, 8·37%.)

A sample of this compound became turbid on standing in contact with laboratory air. It appeared to be hydrolysed by 2 N NaOH solution.

# 7. Preparation of B-tris-(Triphenylsilyl)-N-Trimethylborazene (III)

A solution of triphenylsilyllithium<sup>(13)</sup> freshly prepared from 84 g (0.162 mole) of hexaphenyldisilane and 17 g lithium in 400 ml tetrahydrofuran was added with vigorous stirring to a suspension of 21 g (0.093 mole) of B-trichloro-N-trimethylborazene in 500 ml of diethyl ether at such a rate that a gentle reflux was maintained. The brown colour of the  $(C_0H_5)_3SiLi$  solution was discharged immediately on addition to the (MeNBCl)<sub>3</sub> solution and a white precipitate formed. The mixture was kept at room temperature overnight and then was filtered using a sintered glass filter. The solid was washed with ether and extracted with hot benzene. Evaporation of the benzene left 46 g (55 per cent) of crude product. Recrystallization from benzene and drying *in vacuo* at 70° gave pure B-tris-(triphenylsilyl)-N-trimethylborazene. The substance on heating in a sealed tube under nitrogen appears to shrivel slightly before its melting point of 248–251° is reached.

(Found: C, 75.90; H, 6.23; N, 4.60; B, 3.90; Si, 9.41; mol. wt. (cryoscopic method in benzene), 917. Calc. for  $C_{57}H_{54}N_3B_3Si_3$ : C, 76.25; H, 6.06; N, 4.68; B, 3.61; Si, 9.39% mol. wt., 898.) In the region where absorptions characteristic of the borazene system are found, the infra-red spectrum of III showed the following bands (in cm<sup>-1</sup>): 1434 (s), 1425 (sh), 1377 (s), 1359 (s), 1339 (vs). [( $C_8H_5$ )\_3SiBNMe]\_s is soluble in benzene, chloroform and methylene chloride and poorly soluble in ether and hexane. It decomposes in carbon tetrachloride solution, even in the absence of air. The compound does not appear to be affected by dry air. On being heated in an open test tube it melts to a light yellow liquid which on cooling gives a glassy solid. Heating to higher temperatures (>250°) appears to cause decomposition.

#### Reactions of B-tris-(triphenylsilyl)-N-trimethylborazene

1. Hydrolysis. A solution of 0.3 g of compound III in 30 ml chloroform was shaken with 30 ml of water. The chloroform layer immediately became turbid and methylamine evolution was observed (odour and detection with moist litmus paper). The mixture was shaken for 1 hr and the organic layer was dried over anhydrous calcium chloride. The aqueous phase was alkaline (pH 8–9) and reaction with phenylisothiocyanate indicated the presence of an amine. The infra-red spectrum of the chloroform layer showed a strong band at 2140 cm<sup>-1</sup> (Si-H) as well as bands at 1435 and 1115 cm<sup>-1</sup> [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si] suggesting the presence of triphenylsilane. Weaker absorption in the B-O region was also observed. The remainder of the chloroform solution was evaporated and the residue was extracted with ethanol, leaving a small amount of white powder. The latter was recrystallized twice from hexane and dried *in vacuo* at 40°. This product has not been identified as yet. The ethanol extracts

(18) H. GILMAN and G. D. LICHTENWALTER, J. Amer. Chem. Soc. 80, 608 (1958).

were evaporated at reduced pressure leaving crude triphenylsilane, m.p. 35-41°, identified by comparison of its infra-red spectrum with that of an authentic sample of triphenylsilane.

2. Bromination. A solution of 0.3855 g of compound III in 20 ml of chloroform was prepared and titrated with a chloroform solution of bromine (20.64 mg/ml). A permanent yellow colour due to excess of bromine served as a rough indication of the endpoint. The bromine consumption (10.30 ml of the chloroform solution = 6.19 g atom bromine per mole of compound III) suggested that the initial reaction occurring was

$$[(C_6H_5)_3SiBNMe]_3 + 3Br_2 - 3(C_6H_5)_3SiBr + (BrBNMe)_3$$

The products of the bromination reaction were examined. During the titration a precipitate had formed. This was filtered and tentatively identified as methylammonium bromide,  $[CH_3NH_3]Br$ . It was soluble in water, gave a positive test for halide ion with silver nitrate solution and did not contain boron. It melted at 263–264°, and its infra-red spectrum was consistent with this formulation (Found: C, 11·35; H, 5·40; N, 12·49; Br, 70·49. Calc. for CH<sub>6</sub>NBr: C, 10·73; H, 5·42; N, 12·50; Br, 71·38%.)

Evaporation of the filtrate in vacuum gave a light-tan, crystalline solid, m.p.  $119^{\circ}$ , which could be sublimed in vacuum. Two sublimations gave pure triphenylbromosilane, m.p.  $120-123^{\circ}$  in 56 per cent yield.<sup>(14)</sup> (Found: C, 64.00; H, 4.58; Si, 8.51; Br, 23.46. Calc. for C<sub>18</sub>H<sub>15</sub>BrSi: C, 63.71; H, 4.45; Si, 8.28; Br, 23.55%.)

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<sup>(14)</sup> Melting point reported: 120-121°. P. A. MCCUSKER and E. L. REILLY, J. Amer. Chem. Soc. 75, 1583 (1953).