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Compounds containing B–O–X bonds (X=Si, Ge, Sn, Pb)
Part 5. Synthesis of chain borosilicates containing B:Si ratios of 2:1, 2:2, 2:3 and 2:4. Crystal structure of $(\overline{O{-}CMe_2CH_2CHMe{-}O{-}B}{-}O)_2SiBu^t_2$ [☆]

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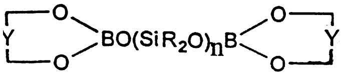
Abstract

Twelve borosilicates with the general formula $\overline{O{-}Y{-}O{-}B}{-}O{-}(SiPh_2O)_n{-}\overline{B{-}O{-}Y{-}O}$ (where $n=1$, 2, 3 or 4; Y=one of the organic groups CMe_2CMe_2, CMe_2CH_2CHMe, $CMe_2CH_2CMe_2$ or $CHPr^iCMe_2CH_2$) were prepared. Three synthetic routes were investigated, including a one-pot self-assembly reaction of two equivalents each of boric acid, silanediol and organic diol. The probable sequence for this reaction is discussed. The borosilicates were either solids or viscous liquids and were colourless. They formed cyclosiloxane species when thermally decomposed or reacted with either water or potassium trimethylsilanolate. They were unreactive to triethylamine, di-iso-propylamine, pyridine or ethylenediamine. The di-tert-butyl species $(\overline{O{-}CMe_2CH_2CHMe{-}O{-}B}{-}O)_2SiBu^t_2$ was prepared and structurally characterised using X-ray techniques. The parameters associated with the B–O–Si bonds were a B–O–Si angle of 141.5(2)° and B–O and Si–O distances of 1.360(4) and 1.625(2) Å, respectively. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Borosilicate; Silyl borate; Synthesis; X-ray crystallography

1. Introduction

Borosilicate materials have found important uses in many areas. As an example of their current significance, one may cite their use as interlayer dielectrics in microelectronics manufacture [2]. However, relatively little is known about the chemistry, and, in particular, the structural chemistry of molecular borosilicates. A research programme has been initiated [1] to investigate these compounds. We now report the syntheses and properties of some borosilicates with $B{-}O{-}(Si{-}O)_n{-}B$ linked structures. The compounds studied are of the general type shown in the diagram below where $n=1$, 2, 3 or 4, Y is one of the organic groups CMe_2CMe_2, CMe_2CH_2CHMe, $CMe_2CH_2CMe_2$ or $CHPr^iCMe_2CH_2$, and R=Ph or Bu^t.



Three synthetic routes to these compounds were used. These may be described as: (a) dehydration reactions between silanediols, boric acid and organic diols, e.g. reactions (1) (3) and (5), (b) dehydration reactions between silanediols and either a 1,3,2-dioxaborolan-2-ol or a borinan-2-ol, e.g. reaction (7), and (c) dehydrochlorination reactions between dichlorosilanes and either a 1,3,2-dioxaborolan-2-ol or a borinan-2-ol, e.g. reactions (8) and (9). The compounds **1**–**13** which were prepared are shown in Table 1.

2. Experimental

All reactions were initially carried out in an inert atmosphere. Work-up of products was carried out in air. Solvents (Aldrich or Merck) were dried and distilled before use. Water was doubly distilled and deionised. The following reagents were used as supplied by Aldrich Chemical

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[☆] D. Murphy, J.P. Sheehan, T.R. Spalding, G. Ferguson, A.J. Lough, J.F. Gallagher, J. Mater. Chem. 3 (1993) 1275.

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Table 1
Borosilicates prepared in the present work

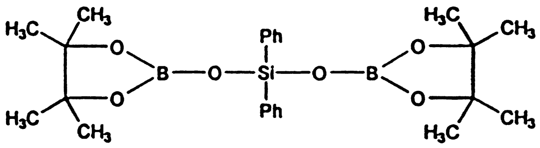
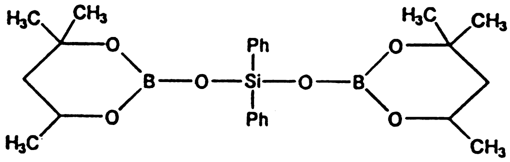
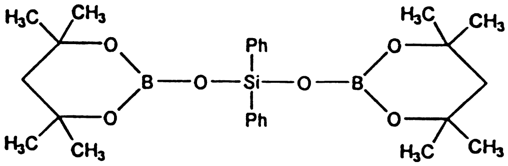
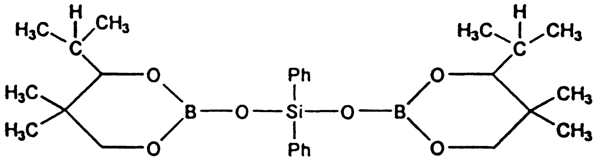
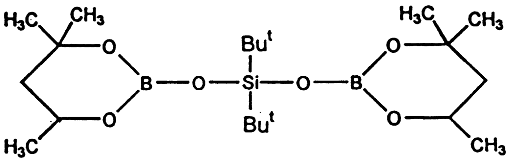
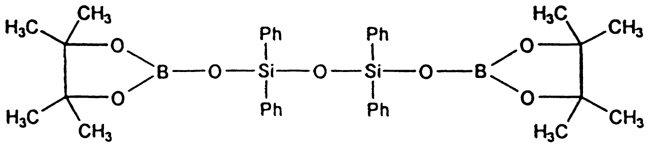
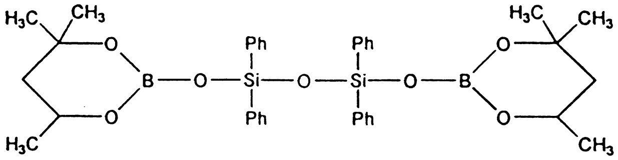
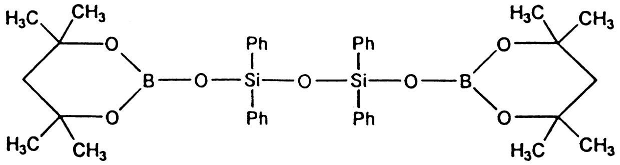
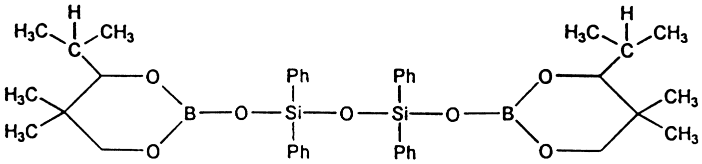
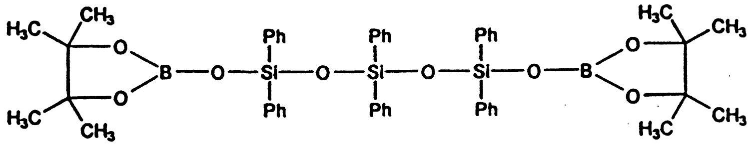
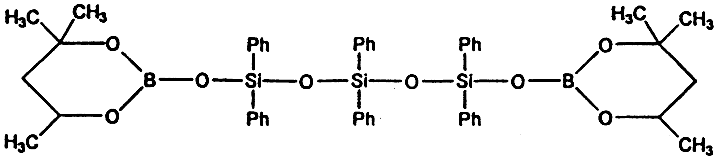
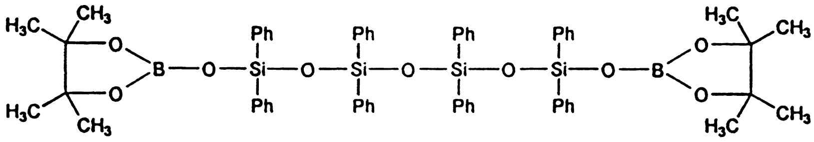
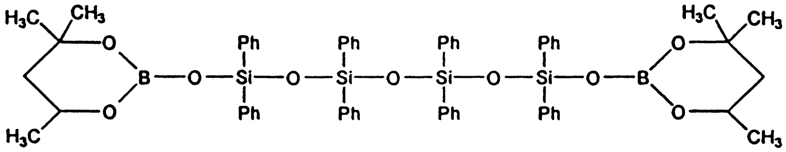
Compound no.	Structure
1	
2	
3	
4	
5	
6	
7	
8	

Table 1. Continued

Compound no.	Structure
9	
10	
11	
12	
13	

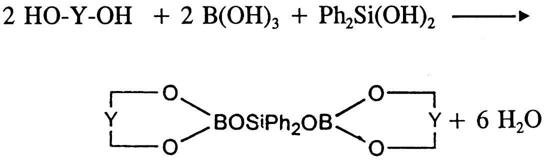
Co.: boric acid, diphenylsilanediol, 2,3-dimethyl-2,3-butanediol, 2,4-dimethyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, dichlorodiphenylsilane, triethylamine, pyridine, di-iso-propylamine, ethylenediamine, potassium trimethylsilanolate, di-tert-butyldichlorosilane; aniline (Merck) and 2-methyl-2,4-pentanediol (BDH) were distilled prior to use and 1,3-dichloro-1,1,3,3-tetraphenyldisiloxane (Fluorochem) was used as supplied. The substituted 1,3,2-dioxaborolan-2-ol (Y=CMe_2CMe_2) and -borinan-2-ols (Y=CMe_2CH_2CHMe, $CMe_2CH_2CMe_2$, $CHPr^iCMe_2CH_2$) were prepared according to literature methods [4]. The 1,1,3,3-tetraphenyldisiloxane-1,3-diol, 1,1,3,3,5,5-hexaphenyltrisiloxane-1,5-diol and 1,1,3,3,5,5-7,7-octaphenyltetrasiloxane-1,7-diol were prepared by literature methods [5].

Infrared spectra in the range 4000–4500 cm^{-1} were recorded on a Perkin-Elmer Paragon 1000 FT spectrometer as KBr discs or thin films between NaCl plates. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent at ambient temperature on a JEOL FT NMR GSX-270 spectrometer using $SiMe_4$ as standard. Mass spectra were recorded on a Kratos Profile mass spectrometer in EI mode. Melting points were recorded on an Electrothermal IA 9000 apparatus and are uncorrected. Elemental analyses were carried out on a Perkin-Elmer 240C analyser by the Microanalytical Laboratory, University College, Cork.

*2.1. Synthesis of compounds **1–4** and **6–13** from an organic diol, boric acid and appropriate silanediol in 2:2:1 ratio*

*2.1.1. Compounds **1–4**: Eq. (1)*

(As identical procedures were followed for the preparations of **1**–**4**, a detailed description is given only for **1**). Compound **1** has been reported previously [3].



(1)

where Y=CMe_2CMe_2, CMe_2CH_2CHMe, $CMe_2CH_2CMe_2$ or $CHPr^iCMe_2CH_2$.

2.1.1.1. *Compound* ***1***

A mixture of 2,3-dimethyl-2,3-butanediol (0.745 g, 6.30 mmol), boric acid (0.390 g, 6.31 mmol) and diphenylsilanediol (0.681 g, 3.15 mmol) was added to 50 ml toluene and the solution was refluxed for 8 h in a Dean–Stark apparatus. Removal of solvent on a rotary evaporator afforded a viscous liquid which was redissolved in hexanes. The solution was filtered to remove small amounts of insoluble powder, concentrated (to ≈8 ml) on a rotary evaporator and cooled to −22°C. After a few hours, compound **1** formed as a colourless solid (1.328 g, 90.1%). Mp 42–45°C. Found: C, 61.73; H, 7.40; B, 4.92%. $C_{24}H_{34}B_2O_6Si$ requires: C, 61.56; H, 7.32; B, 4.62%. IR (KBr disc), ν_{max}/cm^{-1}: 2974(s), 1380(br, vs), 1307(vs), 1212(s), 1178(s), 1121(s), 841(s), 663(s), 510(s). ^1H NMR ($CDCl_3$): 7.73–7.67 [d, 4H, $C_6\underline{\mathbf{H}}_5$]; 7.50–7.29 [m, 6H, $C_6\underline{\mathbf{H}}_5$]; 1.25 [s, 24H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 134.25, 133.32, 130.36, 127.75 [all $\underline{\mathbf{C}}_6H_5$]; 82.91 [$\underline{\mathbf{C}}(CH_3)_2$]; 24.51 [$\underline{\mathbf{C}}H_3$]. MS (EI), *m*/*z*: 468 [$(M)^+$].

2.1.1.2. *Compound* ***2***

Compound **2** was prepared on a 4.66-mmol scale: yield 86.7%. Mp 41–44°C. Found: C, 61.69; H, 7.42; B, 4.40%. $C_{24}H_{34}B_2O_6Si$ requires: C, 61.56; H, 7.32; B, 4.62%. IR (KBr disc), ν_{max}/cm^{-1}: 2976(s), 1385(br, vs), 1302(vs), 1210(s), 1177(s), 1122(s), 842(s), 662(s), 511(s). ^1H NMR ($CDCl_3$): 7.75–7.70 [m, 4H, $C_6\underline{\mathbf{H}}_5$]; 7.41–7.25 [m, 6H, $C_6\underline{\mathbf{H}}_5$]; 4.26–4.17 [m, 2H, $C\underline{\mathbf{H}}(CH_3)$]; 1.76–1.65 [m, 4H, $C\underline{\mathbf{H}}_2$]; 1.53–1.17 [m, 18H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 134.72, 130.18, 129.69, 127.46 [all $\underline{\mathbf{C}}_6H_5$]; 72.15 [$\underline{\mathbf{C}}(CH_3)_2$]; 65.94 [$\underline{\mathbf{C}}H(CH_3)$]; 45.63 [$\underline{\mathbf{C}}H_2$]; 31.12, 27.66, 23.07 [all $\underline{\mathbf{C}}H_3$]. MS (EI), *m*/*z*: 468 [$(M)^+$].

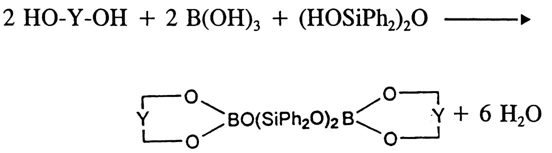
2.1.1.3. *Compound* ***3***

Compound **3** was prepared on a 2.19-mmol scale: yield 79.2%. Bp decomp. at 190°C (3 mmHg). Found: C, 62.66; H, 7.68; B, 4.15%. $C_{26}H_{38}B_2O_6Si$ requires: C, 62.92; H, 7.72; B, 4.36%. IR (thin film), ν_{max}/cm^{-1}: 2975(s), 1369(br, vs), 1303(s), 1209(vs), 1126(s), 718(s), 700(s), 502(s). ^1H NMR ($CDCl_3$): 7.72–7.13 [m, 10H, $C_6\underline{\mathbf{H}}_5$]; 1.73 [s, 4H, $C\underline{\mathbf{H}}_2$]; 1.15 [s, 24H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 135.06, 134.28, 130.03, 127.67 [$\underline{\mathbf{C}}_6H_5$]; 72.42 [$\underline{\mathbf{C}}(CH_3)_2$]; 48.42 [$\underline{\mathbf{C}}H_2$]; 31.45 [$\underline{\mathbf{C}}H_3$]. MS (EI), *m*/*z*: 496 [$(M)^+$].

2.1.1.4. *Compound* ***4***

Compound **4** was prepared on a 7.88-mmol scale: yield 85.2%. Mp 54–56°C. Found: C, 64.01; H, 7.99; B, 3.83%. $C_{28}H_{42}B_2O_6Si$ requires: C, 64.14; H, 8.07; B, 4.12%. IR (KBr disc), ν_{max}/cm^{-1}: 1410(s), 1382(vs), 1299(s), 1209(s), 1179(s), 1125(s), 844(s), 664(s). ^1H NMR ($CDCl_3$): 7.78–7.65 [m, 4H, $C_6\underline{\mathbf{H}}_5$]; 7.41–7.24 [m, 6H, $C_6\underline{\mathbf{H}}_5$]; 3.65–3.31 [m, 6H, $4C\underline{\mathbf{H}}_2$ and $2C\underline{\mathbf{H}}Pr^i$]; 1.91–1.69 [m, 2H, $C\underline{\mathbf{H}}Me_2$]; 1.17–0.66 [m, 24H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 134.70, 129.89, 127.43 [all $\underline{\mathbf{C}}_6H_5$]; 84.53 [$\underline{\mathbf{C}}H_2$–O]; 74.32 [$\underline{\mathbf{C}}HPr^i$]; 34.92, 29.47, 23.50, 22.64 [all $\underline{\mathbf{C}}H_3$]; 18.95 [$\underline{\mathbf{C}}H(CH_3)_2$]; 17.40 [$\underline{\mathbf{C}}(CH_3)_2$]. MS (EI), *m*/*z*: 524 [$(M)^+$].

2.1.2. *Compounds* ***6–9****: Eq. (2)*



(2)

2.1.2.1. *Compound* ***6***

Prepared on a 2.96-mmol scale: yield 93.4%. Mp 74–76°C. Found: C, 65.16; H, 6.56; B, 3.11%. $C_{36}H_{44}B_2O_7Si_2$ requires: C, 64.87; H, 6.65; B, 3.24%. IR (KBr disc), ν_{max}/cm^{-1}: 1428(vs), 1379(s), 1317(vs), 1154(s), 1125(s), 1101(vs), 955(s), 858(s), 803(s), 718(s), 518(vs). ^1H NMR ($CDCl_3$): 7.70–7.66 [d, 8H, $C_6\underline{\mathbf{H}}_5$]; 7.38–7.23 [m, 12H, $C_6\underline{\mathbf{H}}_5$]; 1.26 [s, 24H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 134.99, 134.21, 130.44, 128.08 [all $\underline{\mathbf{C}}_6H_5$]; 83.39 [$\underline{\mathbf{C}}(CH_3)_2$]; 24.81 [$\underline{\mathbf{C}}H_3$]. MS (EI), *m*/*z*: 666 [$(M)^+$].

2.1.2.2. *Compound* ***7***

Compound **7** was prepared on a 2.89-mmol scale: yield 90.7%. Mp 100–102°C. Found: C, 64.66; H, 6.61; B, 3.39%. $C_{36}H_{44}B_2O_7Si_2$ requires: C, 64.87; H, 6.65; B, 3.24%. IR (KBr disc), ν_{max}/cm^{-1}: 1429(s), 1395(vs), 1372(vs), 1303(s), 1125(vs), 1101(s), 838(s), 720(s), 698(s), 518(s). ^1H NMR ($CDCl_3$): 7.71–7.65 [m, 8H, $C_6\underline{\mathbf{H}}_5$]; 7.40–7.23 [m, 12H, $C_6\underline{\mathbf{H}}_5$]; 4.23–4.10 [m, 2H, $C\underline{\mathbf{H}}(CH_3)$]; 1.61–1.51 [m, 4H, $C\underline{\mathbf{H}}_2$]; 1.42–1.06 [m, 18H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 134.77, 129.94, 129.57, 127.49 [all $\underline{\mathbf{C}}_6H_5$]; 72.22 [$\underline{\mathbf{C}}(CH_3)_2$]; 65.93 [$\underline{\mathbf{C}}H(CH_3)$]; 45.45 [$\underline{\mathbf{C}}H_2$]; 30.94, 27.35, 22.89 [all $\underline{\mathbf{C}}H_3$]. MS (EI), *m*/*z*: 666 [$(M)^+$].

2.1.2.3. *Compound* ***8***

Compound **8** was prepared on a 3.62-mmol scale: yield 82.6%. Bp decomp. at 175°C (1.5 mmHg). Found: C, 65.86; H, 6.97; B, 3.33%. $C_{38}H_{48}B_2O_7Si_2$ requires: C, 65.71; H, 6.97; B, 3.11%. IR (thin film), ν_{max}/cm^{-1}: 2975(s), 1369(br, vs), 1210(s), 1123(s), 1097(vs), 861(s), 718(s), 699(s), 511(vs). ^1H NMR ($CDCl_3$): 7.60–7.09 [m, 20H, $C_6\underline{\mathbf{H}}_5$]; 1.69 [s, 4H, $C\underline{\mathbf{H}}_2$]; 1.18 [s, 24H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 135.00, 134.19, 130.09, 127.75 [all

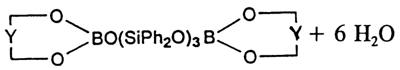
$\underline{\mathbf{C}}_6H_5$]; 72.33 [$\underline{\mathbf{C}}(CH_3)_2$]; 48.88 [$\underline{\mathbf{C}}H_2$]; 31.41 [$\underline{\mathbf{C}}H_3$]. MS (EI), *m/z*: 694 [$(M)^+$].

2.1.2.4. Compound ***9***

Compound **9** was prepared on a 3.62-mmol scale: yield 83.1%. Bp decomp. at 185°C (2 mmHg). Found: C, 66.26; H, 7.19; B, 2.78%. $C_{40}H_{52}B_2O_7Si_2$ requires: C, 66.48; H, 7.25; B, 2.99%. IR (thin film), ν_{max}/cm^{-1}: 1422(s), 1402(s), 1384(vs), 1343(vs), 1126(s), 718(s), 699(s), 518(s). ^1H NMR ($CDCl_3$): 7.68–7.66 [m, 8H, $C_6\underline{\mathbf{H}}_5$]; 7.38–7.23 [m, 12H, $C_6\underline{\mathbf{H}}_5$]; 3.59–3.31 [m, 6H, 4$C\underline{\mathbf{H}}_2$ and 2$C\underline{\mathbf{H}}Pr^i$]; 1.92–1.74 [m, 2H, $C\underline{\mathbf{H}}Me_2$]; 1.03–0.67 [m, 24H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 134.98, 129.93, 127.54 [all $\underline{\mathbf{C}}_6H_5$]; 84.60 [$\underline{\mathbf{C}}H_2$–O]; 74.29 [$\underline{\mathbf{C}}HPr^i$]; 34.93, 29.48, 23.75, 22.66 [all $\underline{\mathbf{C}}H_3$]; 18.95 [$\underline{\mathbf{C}}H(CH_3)_2$]; 17.25 [$\underline{\mathbf{C}}(CH_3)_2$]. MS (EI), *m/z*: 722 [$(M)^+$].

2.1.3. Compounds ***10*** *and* ***11****: Eq. (3)*

$$2\ HO\text{-}Y\text{-}OH + 2\ B(OH)_3 + HO(SiPh_2O)_3H \longrightarrow$$



(3)

where Y=CMe_2CMe_2 or CMe_2CH_2CHMe.

2.1.3.1. Compound ***10***

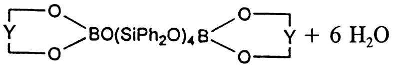
Prepared on a 3.39-mmol scale: yield 75.2%. Bp decomp. at 190°C (1.5 mmHg). Found: C, 66.34; H, 6.35; B, 2.78%. $C_{48}H_{54}B_2O_8Si_3$ requires: C, 66.66; H, 6.29; B, 2.50%. IR (thin film), ν_{max}/cm^{-1}: 1428(vs), 1379(s), 1315(s), 1127(vs), 1075(vs), 858(s), 719(s), 699(s). ^1H NMR ($CDCl_3$): 7.73–7.08 [m, 30H, $C_6\underline{\mathbf{H}}_5$]; 1.21 [s, 24H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 135.24, 134.37, 130.04, 127.54 [all $\underline{\mathbf{C}}_6H_5$]; 82.71 [$\underline{\mathbf{C}}(CH_3)_2$]; 24.47 [$\underline{\mathbf{C}}H_3$]. MS (EI), *m/z*: 864 [$(M)^+$].

2.1.3.2. Compound ***11***

Prepared on a 2.12-mmol scale: yield 77.3%. Bp decomp. at 190°C (1.5 mmHg). Found: C, 66.78; H, 6.32; B, 2.29%. $C_{48}H_{54}B_2O_8Si_3$ requires: C, 66.66; H, 6.29; B, 2.50%. IR (thin film), ν_{max}/cm^{-1}: 1429(s), 1399(vs), 1372(vs), 1304(vs), 1126(vs), 1075(vs), 838(s), 718(s), 699(s), 523(s). ^1H NMR ($CDCl_3$): 7.70–7.08 [m, 30H, $C_6\underline{\mathbf{H}}_5$]; 4.58–4.00 [m, 2H, $C\underline{\mathbf{H}}(CH_3)$]; 1.72–1.49 [m, 4H, $C\underline{\mathbf{H}}_2$]; 1.33–1.01 [m, 18H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 135.24, 134.66, 129.98, 127.59 [all $\underline{\mathbf{C}}_6H_5$]; 72.16 [$\underline{\mathbf{C}}(CH_3)_2$]; 65.92 [$\underline{\mathbf{C}}H(CH_3)$]; 45.55 [$\underline{\mathbf{C}}H_2$]; 30.93, 27.61, 22.88 [all $\underline{\mathbf{C}}H_3$]. MS (EI), *m/z*: 864 [$(M)^+$].

2.1.4. Compounds ***12*** *and* ***13****: Eq. (4)*

$$2\ HO\text{-}Y\text{-}OH + 2\ B(OH)_3 + HO(SiPh_2O)_4H \longrightarrow$$



(4)

where Y=CMe_2CMe_2 or CMe_2CH_2CHMe.

2.1.4.1. Compound ***12***

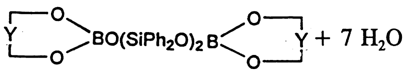
Prepared on a 2.12-mmol scale: yield 78.5%. Bp decomp. at 175°C (2 mmHg). Found: C, 67.55; H, 6.11; B, 1.84%. $C_{60}H_{64}B_2O_9Si_4$ requires: C, 67.79; H, 6.07; B, 2.03%. IR (thin film), ν_{max}/cm^{-1}: 1428(vs), 1379(vs), 1315(s), 1127(s), 1070(vs), 858(s), 719(s), 698(s), 524(s). ^1H NMR ($CDCl_3$): 7.57–6.95 [m, 40H, $C_6\underline{\mathbf{H}}_5$]; 1.13 [s, 24H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 134.52, 133.94, 129.92, 127.52 [all $\underline{\mathbf{C}}_6H_5$]; 82.87 [$\underline{\mathbf{C}}(CH_3)_2$]; 24.44 [$\underline{\mathbf{C}}H_3$].

2.1.4.2. Compound ***13***

Prepared on a 2.12-mmol scale: yield 74.9%. Bp decomp. at 175°C (2 mmHg). Found: C, 67.89; H, 5.99; B, 2.22%. $C_{60}H_{64}B_2O_9Si_4$ requires: C, 67.79; H, 6.07; B, 2.03%. IR (thin film), ν_{max}/cm^{-1}: 1429(s), 1398(s), 1372(vs), 1309(vs), 1126(vs), 1072(vs), 718(s), 699(s), 522(s). ^1H NMR ($CDCl_3$): 7.70–7.05 [m, 40H, $C_6\underline{\mathbf{H}}_5$]; 4.35–3.96 [m, 2H, $C\underline{\mathbf{H}}(CH_3)$]; 1.56–1.42 [m, 4H, $C\underline{\mathbf{H}}_2$]; 1.29–1.01 [m, 18H, $C\underline{\mathbf{H}}_3$]. ^{13}C NMR ($CDCl_3$): 135.20, 134.71, 129.82, 127.77 [all $\underline{\mathbf{C}}_6H_5$]; 72.15 [$\underline{\mathbf{C}}(CH_3)_2$]; 66.00 [$\underline{\mathbf{C}}H(CH_3)$]; 45.53 [$\underline{\mathbf{C}}H_2$]; 30.91, 27.45, 22.88 [all $\underline{\mathbf{C}}H_3$].

2.2. Synthesis of compounds ***6–9*** *from an organic diol, boric acid and diphenylsilanediol in a 1:1:1 ratio on a ≈3-mmol scale*

$$2\ HO\text{-}Y\text{-}OH + 2\ B(OH)_3 + 2\ Ph_2Si(OH)_2 \longrightarrow$$

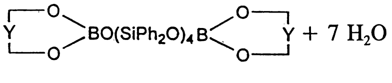


(5)

Compounds **6**–**9** were identified by elemental analysis (C, H, B), infrared spectroscopy, mass spectrometry and, for **6** and **7**, by melting point. The yields of **6**, **7**, **8** and **9** were 88.8, 87.1, 77.0 and 80.0%, respectively.

2.3. Synthesis of ***12*** *and* ***13*** *from an organodiol, boric acid and 1,1,3,3-tetraphenyldisiloxane-1,3-diol in a 1:1:1 ratio on a ≈3-mmol scale*

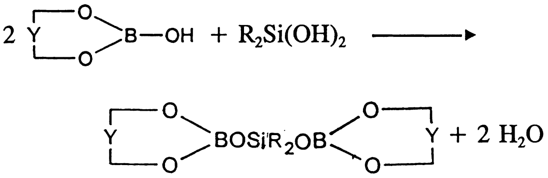
$$2\ HO\text{-}Y\text{-}OH + 2\ B(OH)_3 + 2\ (HOSiPh_2)_2O \longrightarrow$$



(6)

Both compounds **12** and **13** were identified by elemental analysis (C, H, B), IR spectroscopy and ^{1}H NMR spectroscopy. The yields of **12** and **13** were 68.7 and 65.3%, respectively.

2.4. *Synthesis of **1–5** from a 1,3,2-dioxaborolan-2-ol or 1,3,2-borinan-2-ol and the appropriate diorganosilanediol in a 2:1 ratio on a ≈4.65-mmol scale*



(7)

The synthesis of **5** is given as an example; **1–4** were prepared similarly in yields of 88.1, 86.9, 78.4 and 85.0%, respectively. A mixture of 4,4,6-trimethyl-1,3,2-dioxaborinan-2-ol (0.818 g, 5.68 mmol) and di-tert-butylsilanediol (0.501 g, 2.84 mmol) was refluxed for 10 h in toluene (40 ml) in a Dean–Stark apparatus. Removal of solvent gave a viscous liquid which was dissolved in toluene (≈8 ml) and cooled to −24°C. Large colourless crystals of **5** formed after ≈1 day (1.003 g, 82.4%). Mp 51–53°C. Found: C, 56.20; H, 9.92; B, 4.83%. $C_{20}H_{42}B_2O_6Si$ requires: C, 56.09; H, 9.89; B, 5.05%. IR (KBr disc), ν_{max}/cm^{-1}: 1407(s), 1382(vs), 1299(s), 1208(s), 1179(s), 878(s), 844(vs), 769(s), 662(s). ^{1}H NMR ($CDCl_3$): 4.25–4.17 [m, 2H, $C\underline{\mathbf{H}}(CH_3)$]; 1.78–1.46 [m, 4H, $C\underline{\mathbf{H}}_2$]; 1.41–1.21 [m, 18H, $C\underline{\mathbf{H}}_3$ of dioxaborinane rings]; 1.01 [s, 18H, $C\underline{\mathbf{H}}_3$ of tert-butyl groups]. ^{13}C NMR ($CDCl_3$): 72.71 [$\underline{C}(CH_3)_2$]; 66.69 [$\underline{C}H(CH_3)$]; 46.52 [$\underline{C}H_2$]; 32.07, 28.30, 24.08, 21.13 [all $\underline{C}H_3$]. MS (EI), *m/z*: 371 [$(M)^+$–Bu^t].

2.4.1. *X-ray crystallography*

Crystal data, data collection, structure solution and refinement details for **5** are summarised in Table 2. Fig. 1 was prepared with the aid of published crystallographic programmes [6–8]. Full crystallographic details have been deposited in CIF format with the Cambridge Crystallographic Data Centre and are also available directly from the authors.

2.5. *Synthesis of **1–4** from a 1,3,2-dioxaborolan-2-ol or -borinan-2-ol and dichlorodiphenylsilane*

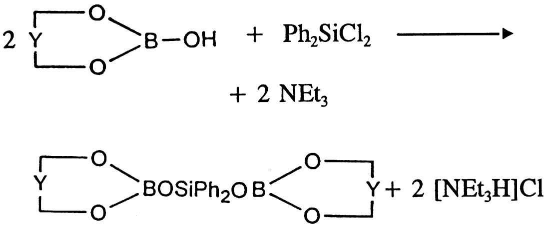
(Only the synthesis of **1**, Y=CMe_2CMe_2, is described in detail. Compounds **2–4** were prepared similarly). The yields of **2**, **3** and **4** were 79.5, 69.3 and 78.8%, respectively.

Table 2
Summary of crystal data, data collection, structure solution and refinement details for **5**

(a) *Crystal data*	
Empirical formula	$C_{20}H_{42}B_2O_6Si$
Molar mass	428.25
Color, habit	Colorless, block
Crystal size, mm	0.38×0.38×0.36
Crystal system	Monoclinic
a, Å	19.346(3)
b, Å	10.1974(10)
c, Å	16.859(2)
β, °	127.810(10)
V, Å^3	2627.6(6)
Space group	*C2/c*
Molecular symmetry	Two-fold
Z	4
F(000)	936
d_{calc}, g cm^{-3}	1.083
μ, mm^{-1}	0.118
(b) *Data acquisition*[a]	
Temperature, K	294(1)
Unit-cell reflections (*θ* range, °)	10.4–16.2
Max. *θ* (°) for reflections	25
hkl range of reflections	−22 to 18; 0 to 12; 0 to 20
Decay in 3 standard reflections	5.4%
Reflections measured	2374
Unique reflections	2296
R_{int}	0.009
Reflections with $I>2\sigma(I)$	1330
(c) *Structure solution and refinement*[b]	
Refinement on	F^2
Solution method	Direct methods
H-atom treatment	Riding
No. of variables in L.S.	132
Weights:	
k in $w=1/(\sigma^2F_o^2+k)$ $[P=(F_o^2+2F_c^2)/3]$	$(0.1120P)^2+0.1060P$
R, R_w, *gof*	0.067, 0.205, 1.08
Density range in final Δ-map, e Å^{-3}	−0.29, +0.43
Final shift/error ratio	0.00

[a] Data collection on an Enraf Nonius CAD4 diffractometer with graphite monochromatised Mo-Kα radiation (λ=0.71073 Å).

[b] Calculations were done on a Dell Inspiron 3200 laptop computer system with the NRCVAX system of programs (E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, P.S. White, J. Appl. Crystallogr. 22 (1989) 384–389) [6] for data reduction and with SHELXL-93 (Sheldrick, 1993) [7] for refinement with all data on F^2.



(8)

2.5.1. *Compound **1***

Triethylamine (0.820 g, 8.10 mmol) in 20 ml ether was added dropwise to a solution of 4,4,5,5-tetramethyl-1,3,2-

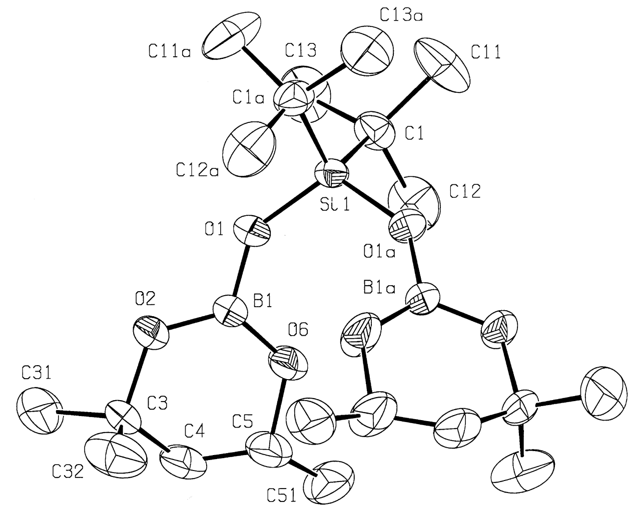
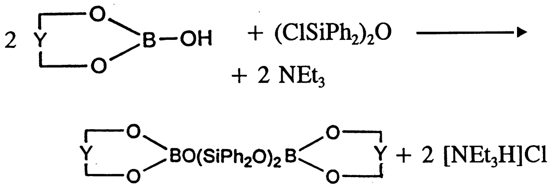


Fig. 1. A general view of **5** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

dioxaborolan-2-ol (1.138 g, 7.90 mmol) and dichlorodiphenylsilane (1.001 g, 3.95 mmol) in 40 ml ether. A white precipitate of $[Et_3NH]Cl$ (1.071 g, 98.4%) (IR) formed immediately. This was removed after 12 h. Removal of solvent afforded a cloudy viscous liquid which was dissolved in hexanes and the solution filtered. The resulting clear solution was concentrated (to $\approx$10 ml) and cooled to -21°C. After 1 day, **1** formed as colourless crystals (1.566 g, 84.6%).

*2.6. Synthesis of **6–9** from a 1,3,2-dioxaborolan-2-ol or -borinan-2-ol and 1,3-dichloro-1,1,3,3-tetraphenyldisiloxane*

(Only **6**, Y$=$$CMe_2CMe_2$, is described. Compounds **7–9** were prepared similarly).



(9)

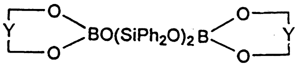
*2.6.1. Compound **6***

Triethylamine (0.260 g, 2.57 mmol) in 20 ml ether was added dropwise to a solution of 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-ol (0.697 g, 4.84 mmol) and 1,3-dichloro-1,1,3,3-tetraphenyldisiloxane (1.093 g, 2.42 mmol) in 40 ml ether. After 12 h, the colourless precipitate of $[Et_3NH]Cl$ was removed by filtration (0.660 g, 99.0%). Removal of solvent afforded a colourless solid which was recrystallised from hot cyclohexane affording **6** as colourless crystals (1.415 g, 87.7%).

Compounds **7–9** were isolated in yields of 85.1, 74.0 and 75.9%, respectively.

*2.7. Attempted synthesis of **10** and **11** from organodiol, boric acid and diphenylsilanediol in a 2:2:3 mol ratio*

$$2\ \text{HO-Y-OH} + 2\ B(OH)_3 + 3\ Ph_2Si(OH)_2 \longrightarrow$$



(10)

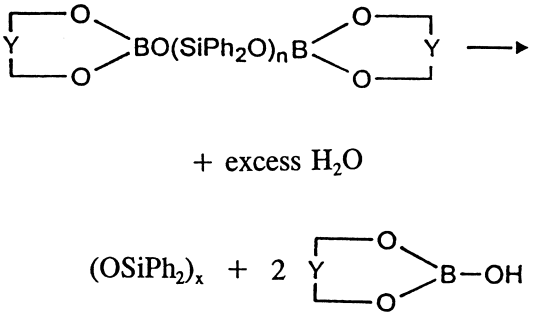
The attempted synthesis of compound **10** by reaction (10) afforded hexaphenyltrisiloxane, $(Ph_2SiO)_3$ (0.210 g, 31.3% based on diphenylsilanediol) and **6** (i.e. a two-silicon chain silyl borate), 1.90 g, 84%. Similar results were obtained when 2-methyl-2,4-pentanediol was used in the attempted synthesis of **11**. In this case, the yield of **7** was 82%.

*2.8. Thermal decomposition reactions of the borosilicates **1–4** and **6–13***

The liquid chain borosilicates **3** and **8–13** decomposed prior to their distillation temperatures affording dark brown decomposition products which solidified at room temperature. Attempted fractional recrystallisation of these solids was unsuccessful. However, their IR spectra contained significant bands in the region 1100–1040 cm^{-1}, consistent with the presence of Si–O–Si bonds [9]. Examination of these spectra suggested the presence of $(Ph_2SiO)_3$, **14**, as the predominant siloxane product when one- or three-silicon borosilicate compounds were decomposed and $(Ph_2SiO)_4$, **15**, when two- or four-silicon compounds were decomposed. Supporting evidence was obtained in the mass spectra of the decomposition products {parent ions at $m/z=594$ and 792 for **14** and **15**, respectively}. The IR spectra of decomposition products also contained peaks in the region 1400–1375 cm^{-1} which may be attributed to B–O(–C) stretching [3] and near 3400 cm^{-1} due to B–O(–H) stretching [4].

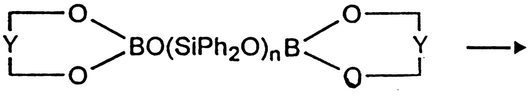
Similar results were obtained for the thermal decompositions of the solid compounds **1**, **2** and **4–7**. Solid samples were heated to 300°C in a melting point apparatus and cooled to room temperature. The brown solid products had the same IR spectral features as those of the products from decomposition of the liquid borosilicates.

*2.9. Reactions of **1–4** and **6–13** with water*



(11)

$Y = CMe_2CMe_2$ or CMe_2CH_2CHMe, $n = 1$, 2, 3 or 4, $x = 3$ or 4.



$$+ \text{ excess } H_2O$$

$$(OSiPh_2)_x + 2\,B(OH)_3 + 2\,\text{HO-Y-OH} \qquad (12)$$

$Y = CMe_2CH_2CMe_2$ or $CHPr^iCMe_2CH_2$, $n = 1$ or 2, $x = 3$ or 4.

2.9.1. $Y = CMe_2CMe_2$ or CMe_2CH_2CHMe, $n = 1–4$, reaction (11)

Solutions of the borosilicates in water/acetone (3:1 v/v) were heated at reflux for 3 h. The solvent was removed affording a colourless solid. Fractional crystallisation gave solids which were identified by mp, IR and mass spectra as $(Ph_2SiO)_3$ (when $n = 1$ or 3), or $(Ph_2SiO)_4$ (when $n = 2$ or 4). The yields of the cyclosiloxanes were quantitative. From each reaction a second colourless solid was isolated and identified by IR and mp as 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-ol or 4,4,6-trimethyl-1,3,2-dioxaborinan-2-ol [4]. The yields of these compounds were quantitative.

2.9.2. $Y = CMe_2CH_2CMe_2$ or $CHPr^iCMe_2CH_2$, $n = 1,2$: reaction (12)

Solutions of the silyl borates in water/acetone (3:1 v/v) were heated at reflux for 3 h. The solvent was removed leaving sticky solids. Ether was added and a powder formed. This was identified as boric acid by IR spectroscopy. The filtrate was concentrated and layered with cyclohexane. Colourless crystalline solids formed which were identified as $(Ph_2SiO)_3$ when $n = 1$ or 3, or, as $(Ph_2SiO)_4$ when $n = 2$ or 4. The solvent was removed from the remaining solution to leave a viscous clear liquid which was identified as either $HOCMe_2CH_2CMe_2OH$ or $HOCHPr^iCMe_2CH_2OH$ by IR spectroscopy. The yields of boric acid, cyclosiloxane and organic diol obtained from hydrolysis reactions (12) were almost quantitative.

2.10. Reactions of **1–4** and **6–13** with potassium trimethylsilanolate

One equivalent of chain silyl borate and one equivalent of $K[OSiMe_3]$ were stirred in dichloromethane solution for 8 h. Removal of solvent left sticky solids or viscous liquids containing suspended solid particles. Fractional crystallisation of these residues from CH_2Cl_2/cyclohexane solutions afforded either $(Ph_2SiO)_3$ (from reactions of compounds containing one or three silicon atoms) or $(Ph_2SiO)_4$ (from compounds with two or four silicon atoms). The yields of cyclosiloxanes were greater than 90%. In the case of solid silyl borates, a second solid was isolated and identified as unreacted silyl borate by IR spectroscopy.

3. Results and discussion

Two borosilicates which contain $O_2B–OSiPh_2O–BO_2$ units have been previously reported [3]. One was compound **1**, a 1,3,2-dioxaborolane derivative (Table 1) and the other was the 2-methyl-1,3,2-dioxaborinane derivative. The present work reports the first examples of chain disilatrioxy-, trisilatetroxy- and tetrasilapentoxy-bridged 1,3,2-dioxaborolanes and -borinanes (Table 1). Compounds **1–4** were prepared by the three different reactions shown in Eqs. (1,7,8). Reaction (1) involved heating a toluene solution of a mixture of two equivalents of the particular organic diol (HO–Y–OH) with two equivalents of boric acid and one equivalent of diphenylsilanediol at reflux temperature in a Dean–Stark apparatus for 8 h. Alternatively, a 1,3,2-dioxaborolan-2-ol or -borinan-2-ol was synthesised initially then reacted with diphenylsilanediol, reaction (7), to give the borosilicate. As the yields from reaction (7) were almost identical to those from reaction (1), the borosilicates **1–4** were more efficiently prepared according to reaction (1), as it is a one-pot reaction. This is an example of an unusual self-assembly reaction involving five separate molecules. The implications of this and some related reactions are discussed below.

The possibility of obtaining the borosilicates **1–4** from dichlorodiphenylsilane was also investigated (Eq. (8)). This reaction involved the addition of two equivalents of triethylamine to an ether solution containing one equivalent of dichlorodiphenylsilane and two equivalents of the particular 1,3,2-dioxaborolan-2-ol or -borinan-2-ol. The yields from reaction (8) were 5–10% lower than for reactions of the type shown in Eqs. (1) and (7). It is also noteworthy that the pinacol derivative **1**, which was previously reported to be a viscous liquid [3], was obtained in the present work as a solid melting at 42–45°C.

Apart from melting points/boiling points, compounds **1–4** were characterised by elemental analysis (C, H and B), IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. The IR spectra of **1–4** exhibited strong absorptions corresponding to the B–O(–Si) stretch [3,10,11] at 1307, 1302, 1303 and 1299 cm^{-1}, respectively. The mass spectra of **1–4** showed the parent ions at $m/z = 468$, 468, 496 and 524, respectively. Peaks arising from the loss of methyl and phenyl groups were common to all four spectra. No unusual ^1H or ^{13}C NMR signals were observed in the spectra of **1–4**. Unfortunately, crystals of the solid compounds **1**, **2** and **4** suitable for X-ray crystallographic analysis could not be obtained.

The synthesis and characterisation of the disilatrioxy-bridged borosilicates **6–9** were achieved in an exactly analogous manner to **1–4**. Compounds **6–9** were obtained from either of the routes shown in Eqs. (2) and (9) {where Y was CMe_2CMe_2, CMe_2CH_2CHMe, $CMe_2CH_2CMe_2$ or $CHPr^iCMe_2CH_2$, respectively}. The yields of compounds **6–9** from reaction (2) were in the range 93–83%. Reaction (9) gave slightly worse results by 5–10%.

An alternative route to **6–9** which involved assembling six reagent molecules was developed and is shown as reaction (5). One advantage of reaction (5) over reaction (2) is that it does not require the use of 1,1,3,3-tetraphenyldisiloxane-1,3-diol, which must first be synthesised from 1,3-dichloro-1,1,3,3-tetraphenyldisiloxane or from dichlorodiphenylsilane. Yields from reaction (5) were in the range 89–77%.

The infrared spectra of **6–9** showed the B–O(–Si) stretch at 1317, 1303, 1302 and 1343 cm^{-1}, respectively. Absorptions of medium to very strong intensity between ≈1100 and 1090 cm^{-1}, which are not observed in the mono-silicon compounds **1–4**, are assigned to Si–O–Si stretching vibrations in **6–9** [9]. The mass spectra of **6–9** showed parent ion peaks and fragmentation patterns largely analogous to those for the single silicon species **1–4**.

Compounds **10** and **11** were prepared in yields of 75 and 77%, respectively, according to reaction (3) {Y= CMe_2CMe_2 or CMe_2CH_2CHMe}.

Attempts to prepare **10** and **11** using three equivalents of diphenylsilanediol, two of boric acid and two of the organic diol in reactions analogous to (5) afforded only the two-silicon compounds **6** and **7**, respectively, and $(Ph_2SiO)_3$. Both **10** and **11** were isolated from reaction (3) as viscous liquids which decomposed when vacuum distillation (≈190°C, 1.5 mmHg) was attempted. Both compounds were identified on the basis of elemental analysis (C, H and B), IR, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The infrared spectra of **10** and **11** contained the B–O(–Si) stretch at 1315 and 1304 cm^{-1}, respectively. The compounds showed parent ion peaks in their mass spectra and the fragmentation patterns were analogous to those of the two-silicon species, **6** and **7**.

Compounds **12** and **13** were prepared in yields of 79 and 75%, respectively, according to reaction (4) {Y= CMe_2CMe_2 or CMe_2CH_2CHMe}.

An alternative synthesis of **12** and **13** was also developed and is given in Eq. (6). The advantage of this method is that it does not require the prior synthesis of the tetrasiloxanediol **8**. However, the yields of reaction (6) were ≈10% lower than those from reaction (4). Compounds **12** and **13** were isolated as viscous liquids which decomposed when vacuum distillation (≈175°C, 2 mmHg) was attempted. Both compounds were identified on the basis of elemental analysis (C, H and B), IR which contained the B–O(–Si) stretch at 1315 and 1309 cm^{-1}, respectively, and ^{1}H and ^{13}C NMR spectroscopy. Attempts to prepare **12** and **13** using four equivalents of diphenylsilanediol in reactions analogous to Eq. (5) afforded only the two-silicon analogues **6** and **7**, respectively, and $(Ph_2SiO)_3$.

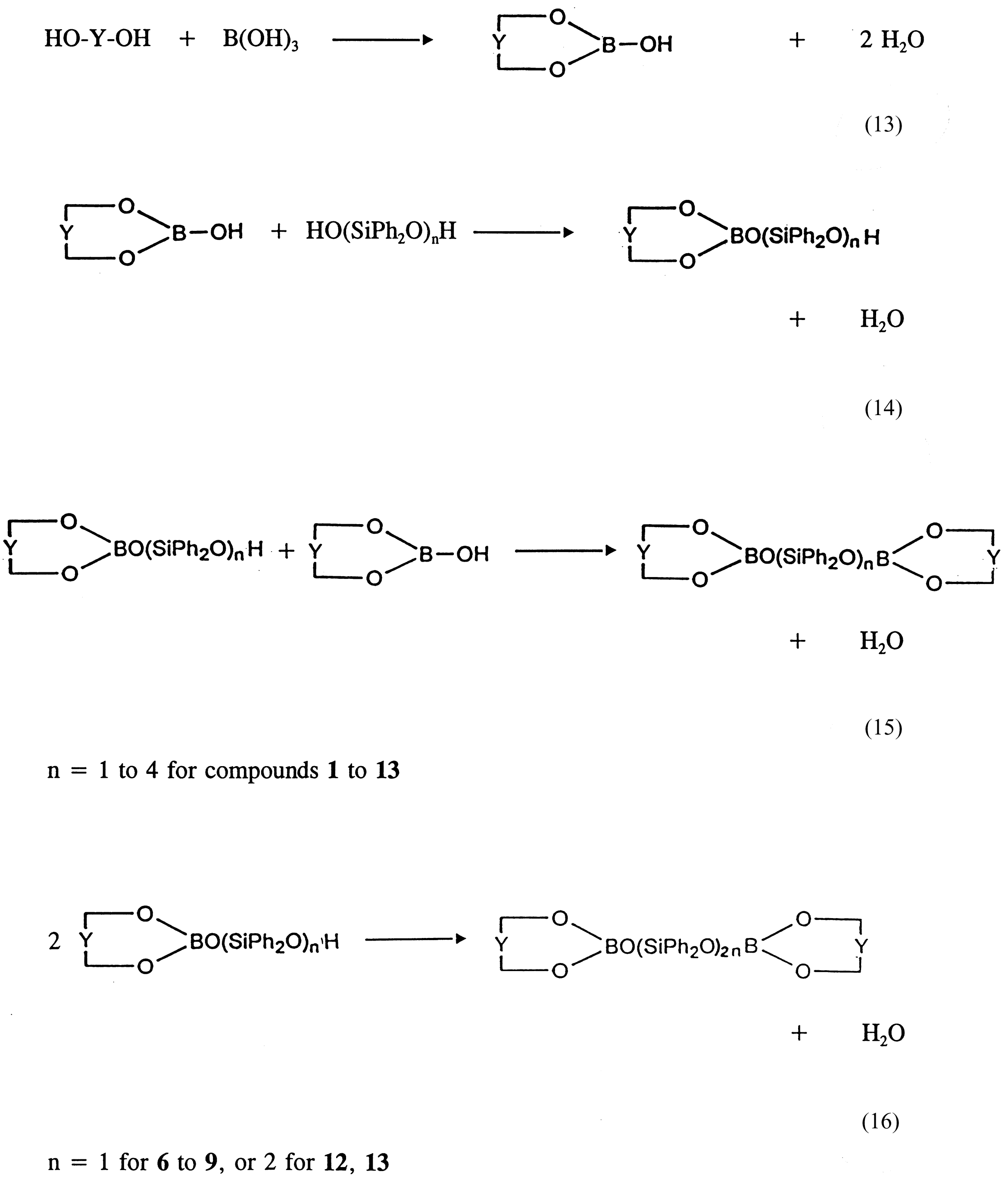
Bearing in mind that in the dehydration reactions, e.g. Eqs. (1) and (5), either five or six molecules, respectively, are assembled to form the borosilicate product in high yield, some comments on the possible sequence of reactions affording the borosilicates are necessary. The most probable sequence is shown in Scheme 1 below. Initially, the 1,3,2-dioxaborolan-2-ol or 1,3,2-dioxaborinan-2-ol is formed from boric acid and the organic diol (Eq. (13)). The next step is the reaction between one equivalent of either the 1,3,2-dioxaborolan-2-ol or 1,3,2-dioxaborinan-2-ol and one equivalent of the silanediol or siloxanediol to produce B–O–Si bonded species which retain one Si–OH moiety (Eq. (14)). The last steps are shown in Eqs. (15) and (16). Evidence supporting the Scheme includes: (a) the lack of any cyclic products containing –Si–O–B–O–Si– units which might be expected if more than one reactive B–OH site was available for reaction with the Si–OH bonds, (b) that yields of products from reactions with mixtures of boric acid and organic diol, or from preformed 1,3,2-dioxaborolan-2-ol or 1,3,2-dioxaborinan-2-ols, are very similar, (c) the isolation of the same products when either two equivalents of $Ph_2Si(OH)_2$ or one of $(HO)SiPh_2OSiPh_2(OH)$ was used (and likewise when two $HO(SiPh_2O)_2H$ or one $HO(SiPh_2O)_4H$ was used), and (d) the formation of two-silicon products **6** and **7**, but not any three-silicon product, when three equivalents of $Ph_2Si(OH)_2$ were used (Eq. (10)).

The preference for Si–OH bonds to react with B–OH rather than other silanol bonds during the self-assembly reactions has been seen previously in the synthesis of the 17-membered cage compound $[B(OSiPh_2OSiPh_2O)_3B]$, **16** [12]. This compound can be prepared in almost identical yields from two moles of boric acid and either six moles of $Ph_2Si(OH)_2$ or three moles of $HOSiPh_2OSiPh_2OH$.

The stability of the chain borosilicates to atmosphere and heat was assessed. The solid compounds **1**, **2** and **4–7** were unchanged after exposure to atmosphere for 2 months. Liquid borosilicates **3** and **8–13** were less stable to atmosphere and after exposure for ≈2 weeks, small amounts of crystalline material began to form. These solids were identified as the cyclosiloxane species $(Ph_2SiO)_3$ (from one- and three-silicon borosilicates) or $(Ph_2SiO)_4$ (from two- and four-silicon borosilicates).

All the liquid chain borosilicates decomposed when vacuum distillation was attempted at ≈170–190°C and 1.5–3 mmHg. Infrared spectral analysis of the products of decomposition indicated the presence of Si–O–Si groups and suggested that the decomposition mixtures contained cyclosiloxane species. Similarly, after the solid compounds had been heated to 300°C, the resulting materials had IR spectra suggestive of cyclosiloxane formation, possibly $(Ph_2SiO)_3$ or $(Ph_2SiO)_4$.

All the borosilicates were decomposed in a refluxing water/acetone (3:1 v/v) solution within 3 h. From compounds containing CMe_2CMe_2 or CMe_2CH_2CHMe moieties, the products were the corresponding 1,3,2-diox-



Scheme 1.

aborolan-2-ol, or borinan-2-ol, and cyclosiloxanes, viz. $(Ph_2SiO)_3$ when $n=1$ or 3, or $(Ph_2SiO)_4$ when $n=2$ or 4 (Eq. (11)). For the chain compounds containing $CMe_2CH_2CMe_2$ or $CHPr^iCMe_2CH_2$ groups, further decomposition occurred during the hydrolysis and the products were the organic diol reagent, boric acid and $(Ph_2SiO)_3$ (for $n=1$) or $(Ph_2SiO)_4$ (for $n=2$) (Eq. (12)).

The tendency for the chain borosilicates **1**–**13** to decompose to siloxane species when exposed to heat or moisture is not a new observation. For example, 'ring-reorganisation' reactions of $(PhBO)(Ph_2SiO)_2$, **17**, and $(PhBO)(Me_2SiO)_2$, **18**, have previously been reported [13]. In the presence of acidic or basic initiators at elevated temperatures, compounds **17** and **18** were converted to siloxane polymers and $(PhBO)_3$. The release of ring strain, coupled with the formation of stable siloxane and boroxine products, were the reasons suggested to explain these observations [13]. In the cases of **1**–**13**, the decompositions may be favoured by the formation of stable siloxane species but the release of ring strain cannot be a factor.

Compounds **1**–**13** were surprisingly unreactive to the following amines even under forcing conditions; triethylamine, di-iso-propylamine, pyridine and ethylenediamine. For example, the borosilicates were recovered unchanged after refluxing in NEt_3, $NHPr^i_2$, pyridine or ethylenediamine for one day. The highly nucleophilic reagent, $K[OSiMe_3]$, easily cleaved the B–O–Si bonds in compounds **1**–**13**. However, the reactions were not selective. Reaction of any chain borosilicate with one equivalent of $K[OSiMe_3]$ afforded either $(Ph_2SiO)_3$ or $(Ph_2SiO)_4$, some unreacted borosilicate and an unidentified sticky colourless solid.

*3.1. Structural characterisation of **5***

Compound **5** was isolated in 82% yield as a colourless solid with melting point 51–53°C. The IR spectrum of **5** contained a strong peak corresponding to the B–O(–Si) stretch at 1299 cm^{-1}. The EI mass spectrum of **5** did not show the parent molecular ion, but the peak at highest mass was at $m/z = 371$, corresponding to the loss of one butyl group.

Compound **5** is the third silyl borate containing the $B–O–Si(Bu^t)_2$ moiety to be studied using X-ray crystallography. Previously, two cyclic compounds had been reported $(PhBO)_2(Bu^t_2SiO)_2$, **19** [14], and $F\overline{BOSiBu^t_2OSiMe_2OSiBu^t_2O}$, **20** [15]. Other compounds of interest are the cage compound $[Bu^tSi\{OB(p\text{-}C_6H_4Br)O\}_3SiBu^t]$, **21** [16], which contains $B–O–Si(Bu^t)$ linkages, and $\overline{O–CMe_2CH_2CH(Me)–O–B}–OSiPh_3$, **22** [17].

Crystals of **5** which were suitable for X-ray diffraction studies were grown from toluene solution at −24°C. Molecules of **5** lie on crystallographic two-fold axes with two symmetry-related trigonal planar BO_3-units bridged by a tetrahedral $Bu^t_2SiO_2$-unit (Fig. 1).

Principal dimensions are given in Table 3. There were no untoward intermolecular contacts. The two independent B–O(C) distances in **5** are essentially identical (1.331(4) and 1.330(5) Å, Table 3), but the B–O(Si) distance is significantly longer (1.360(4) Å). The $B–O(SiBu^t_2)$ distances in **19**, 1.350(4) and 1.350(5) Å [14], are similar to **5** but the distances in **20** are significantly smaller at 1.313(2) and 1.320(3) Å [15]. The $B–O(SiBu^t)$ lengths in the cage compound **21** were in the range 1.345(9)–1.372(10) Å [16]. The B–O(C) distances in **5** (1.330(5), 1.331(4) Å) are shorter than the corresponding distances in **22** (1.347(5), 1.361(5) Å) [17]. The Si–O distance in **5** (1.625(2) Å) is similar to the corresponding distances in **19** [14] (1.630(3), 1.631(2) Å) and **20** [15] (1.626(1), 1.635(2) Å).

The unique B–O–Si angle in **5** measures 141.5(2)° and lies within the range of reported values for such angles, i.e. 128.89(14)° in $(PhBO)(Ph_2SiO)_2$, **17** [13], to 160.9(3)° in $(PhBO)_2(Ph_2SiO)_2$, **23** [18]. The B–O–Si angle in $\overline{O–CMe_2CH_2CH(Me)–O–B}–OSiPh_3$, **22**, was 133.1(2)° [17]. The $B–O–Si(Bu^t_2)$ angles in $(PhBO)_2(Bu^t_2SiO)_2$, **19** [14], and $F\overline{BOSiBu^t_2OSiMe_2OSiBu^t_2O}$, **20** [15], varied from 149.1(3)° in **19** to 159.8(2)° in **20** and are significantly larger than those in **5**. The six $B–O–Si(Bu^t)$ angles in the cage compound $[Bu^tSi\{OB(p\text{–}C_6H_4Br)O\}_3SiBu^t]$, **21** [16], varied from 137.5(6)° to 140.7(6)°.

The unique C_3BO_2 ring in **5** adopts a conformation which is intermediate between a half-chair and a sofa and has dimensions which are very similar to those for this ring in **22** [17].

Table 3
Bond distance and angle data for $(\overline{O–CMe_2CH_2CHMe–O–B}–O)_2SiBu^t_2$, **5**

Bond	Bond length (Å)	Bond	Bond length (Å)
Si1–O1	1.625(2)	C1–C12	1.552(6)
Si1–C1	1.867(4)	C1–C13	1.549(5)
B1–O1	1.360(4)	C3–C4	1.479(5)
B1–O2	1.331(4)	C3–C31	1.507(6)
B1–O6	1.330(5)	C3–C32	1.511(6)
C3–O2	1.443(4)	C4–C5	1.399(6)
C5–O6	1.438(5)	C5–C51	1.494(6)
C1–C11	1.524(5)		

Bond angle	Degrees	Bond angle	Degrees
O1–Si1–O1[a]	112.1(2)	O2–C3–C4	109.4(3)
O1–Si1–C1	107.75(14)	O2–C3–C31	105.4(3)
O1–Si1–C1[a]	105.51(14)	O2–C3–C32	107.0(3)
C1–Si1–C1[a]	118.3(3)	O6–C5–C4	111.1(4)
Si1–C1–C11	112.7(3)	O6–C5–C51	107.3(4)
Si1–C1–C13	111.4(3)	C11–C1–C12	108.0(4)
Si1–C1–C12	107.3(3)	C11–C1–C13	109.6(4)
Si1–O1–B1	141.5(2)	C12–C1–C13	107.6(4)
O1–B1–O2	117.6(3)	C3–C4–C5	119.5(4)
O1–B1–O6	118.7(3)	C4–C3–C31	110.0(4)
O2–B1–O6	123.6(3)	C4–C3–C32	112.0(4)
B1–O2–C3	121.3(3)	C4–C5–C51	119.4(5)
B1–O6–C5	120.5(3)	C31–C3–C32	112.7(4)

[a] This superscript in an atom label refers to equivalent position $-x, y, 1/2 - z$.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition number CCDC 118704.

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References

[1] D. Murphy, J.P. Sheehan, T.R. Spalding, G. Ferguson, A.J. Lough, J.F. Gallagher, J. Mater. Chem. 3 (1993) 1275.
[2] W.S. Rees, in: CVD of Nonmetals, VCH, New York, 1996.
[3] P.N. Bhardwaj, G. Srivastava, J. Indian Chem. Soc. 59 (1982) 300.
[4] H. Steinberg, in: Organoboron Chemistry, Vol. 1, Interscience, New York, 1964.
[5] T.G. Selin, US Patent 4,003,917, 1977.
[6] E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, P.S. White, J. Appl. Crystallogr. 22 (1989) 384.
[7] G.M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.
[8] C.K. Johnson, ORTEP – A Fortran Thermal Ellipsoid Plot Program, Oak Ridge National Laboratory, 1976, Technical Report ORNL-5138.
[9] R.M. Silverstein, G.C. Bassler, T.C. Morrill, in: Spectrometric Identification of Organic Compounds, 4th ed, Wiley, New York, 1981.
[10] E.W. Abel, A. Singh, J. Chem. Soc. (1959) 690.
[11] A.B. Goel, V.D. Gupta, J. Organomet. Chem. 77 (1974) 183.
[12] A.T. O'Dowd, T.R. Spalding, G. Ferguson, J.F. Gallagher, D. Reed, J. Chem. Soc., Chem. Commun. (1993) 1816.
[13] D.A. Foucher, A.J. Lough, I. Manners, Inorg. Chem. 31 (1992) 3034.
[14] A. Mazzah, A. Haoudi-Mazzah, M. Noltemeyer, H.W. Roesky, Z. Anorg. Allg. Chem. 604 (1991) 93.
[15] O. Graalmann, U. Klingebiel, W. Clegg, M. Haase, G.M. Sheldrick, Z. Anorg. Allg. Chem. 519 (1984) 87.
[16] G. Ferguson, B.J. O'Leary, D.M. Murphy, T.R. Spalding, J. Organomet. Chem. 526 (1996) 195.
[17] G. Ferguson, A.J. Lough, J.P. Sheehan, T.R. Spalding, Acta Crystallogr., Sect. C 46 (1990) 1252.
[18] B.J. Brisdon, M.F. Mahon, K.C. Molloy, P.J. Schofield, J. Organomet. Chem. 436 (1992) 11, and references therein.