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MIXED BORYL SILYL AMINES

G. SRIVASTAVA
Chemical Laboratories, University of Rajasthan, Jaipur-4 (India)
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Summary

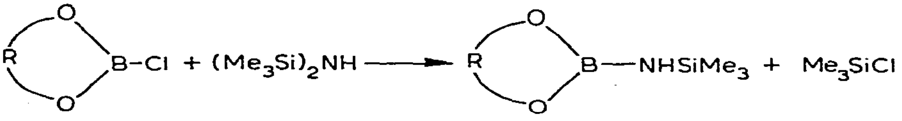
The reactions of bis(trimethylsilyl)amine and tris(trimethylsilyl)amine with 2-chloro-1,3,2-dioxaborolane and 2-chloro-4,4,6-trimethyl-1,3,2,-dioxaborinane have been studied.

Introduction

The silicon—nitrogen bond is readily cleaved by chloroboranes with the formation of a boron—nitrogen bond [1]. Thus, bis(trimethylsilyl)amine has been brought into reaction with BCl_3 [2,3], R_2BCl [4], $PhB(NMe_2)Cl$ [5] and 2-chloro-1,3,2-benzodioxaborole [6]. However, similar cleavage reactions of tris(trimethylsilyl)amine have been little studied [7]. We describe below the reactions of bis(trimethylsilyl)amine and tris(trimethylsilyl)amine with 2-chloro-1,3,2-dioxaborolane and 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane.

Results and discussion

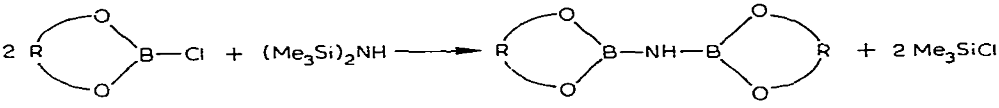
2-(Trimethylsilylamino)-1,3,2-dioxaborolane (I) and 2-(trimethylsilylamino)-4,4,6-trimethyl-1,3,2-dioxaborinane (II) were obtained in quantitative yield by the exothermic reactions between bis(trimethylsilyl)amine and the corresponding 2-chloro derivatives. In contrast to 2-amino-1,3,2,-dioxaborolanes, which are generally polymeric solids [8], these compounds (I) and (II) are colourless volatile liquids.



(I), R = —CH_2—CH_2—

(II), R = —CMe_2—CH_2—CHMe —

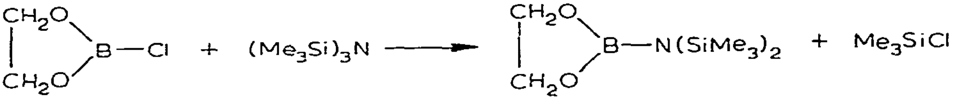
Reactions of bis(trimethylsilyl)amine with 2 moles of chloroboranes were also carried out to give the diborylamines, a comparatively less studied class of compounds [9].



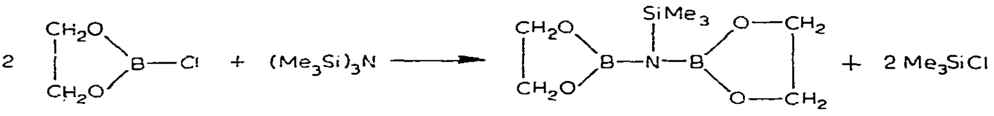
(III) $R = -CH_2-CH_2-$
(IV) $R = -CMe_2-CH_2-CHMe-$

In case of 2-chloro-1,3,2-dioxaborolane, an impure sample of (III) (containing 4% chlorine) was obtained as a white polymeric solid, insoluble in organic solvents. A similar derivative, bis(1,3,2-dioxaborinan-2-yl)amine, $(\overline{O-(CH_2)_3-O-B})_2NH$, has been described previously as an intractable compound [10]. The bisborylamine (IV), however, is a volatile liquid [11].

Tris(trimethylsilyl)amine also reacts exothermally with 2-chloro-1,3,2-dioxaborolane and one trimethylsilyl group is readily cleaved at room temperature with the formation of (1,3,2-dioxaborolan-2-yl)bis(trimethylsilyl)amine (V). For the cleavage of a second trimethylsilyl group the process of heating and removing the liberated trimethylchlorosilane has to be repeated. The mixed derivative (VI) is distilled in a comparatively low yield leaving a polymeric residue.



(V)



(VI)

An unsuccessful attempt has been made to prepare the triborylamine, $(\overline{OCH_2CH_2OB})_3N$, by using more forcing conditions. The amount of polymeric residue increased further and only a small amount of distillate, b.p. 65 - 70°/0.2 - 0.25 mm, was obtained which appears to be mainly 2-(2-chloroethoxy)-1,3,2-dioxaborolane, $\overline{O-CH_2-CH_2-O-B}-OCH_2CH_2Cl$ on the basis of boron analysis and PMR spectrum. Signals for Me_3Si protons as well as the singlet at τ 5.85 (observed in 2-chloro-1,3,2-dioxaborolane) are missing. The spectrum shows a singlet at τ 6.12 and two doublets (J 6 Hz) centered at τ 5.95 and τ 6.4.

Reactions of 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane with tris(trimethylsilyl)amine are comparatively slow and the reaction mixture has to be heated for longer periods. During this process the chloroborane, which is highly

TABLE 1

IR DATA

(I)	(II)	(IV)	(V)	(VI)	Assignment
3425sh	3430w	3440w			ν(N—H)
3360w	3370sh				
2965vs	2980vs	2980vs	2960vs	2960vs	ν(C—H)
2910s	2920s	2940s	2900s	2910s	
		2920s			
1500-1470vsb	1460-1360vsb	1470-1455vsb	1485vs	1485vs	ν(B—N)
1430-1400vsb		1365vs	1420s	1420-1410vs	$\delta(CH_2)$
1385vs			1385vs	1390m	
				1380m	
1362vs	1330s		1345vs	1400-1330vsb	ν(B—O)
1350vs	1310s	1310s			
	1280m	1280m			
	1265m				
1255vs	1250vs		1255vs	1250vs	
	1230w	1230w			$\delta[CH_3(Si)]$ $(CH_3)_2C$
	1210s	1210s			
1195m			1195m	1220s	
				1200w	
1160s				1160vw	
				1110vw	
1065vs	1180s	1170vs	1080s	1070vs	ν(C—O)
1025m	1100w	1105w	1040m	1030s	
	1070w	1070w			
	1010w				
		1025w			C—C
950w				950w	
910vs	910sh	900w	910vs	910vs	
	890s				
	880s				
845vs	860sh		850vs	840vs	$\rho_{as}[CH_3(Si)]$
	840vs				
760m	760m		770m	770s	$\rho_s[CH_3(Si)]$
	750w				
700m	690w		690s	690s	
665s	665m		665s	665m	$\nu_{as}(SiC_3)$
635w	630w		630m	630m	$\nu_s(SiC_3)$

sensitive to temperature, is decomposed to give several fractions on distillation. No attempt was made to separate and identify these.

The identity of the new compounds, (I) — (VI) was further confirmed by PMR (in CCl_4) and IR (neat liquid) spectral study (Table 1). The ν(N—H) peaks appear to indicate that association in the neat form decreases in the order (I) > (II) > (IV). The region between 1500 - 1250 cm^{-1} in all the compounds is very complex showing very strong broad absorptions and unequivocal assignments for B—O and B—N stretching modes are very difficult. In 2-amino-1,3,2-dioxaborolanes [8], the B—N stretching frequencies were tentatively assigned in the region 1530 - 1545 cm^{-1} and the B—O stretching frequencies in the region 1302 - 1230 cm^{-1}, thus assuming a higher than normal B—N bond order and a lower than normal B—O bond order. In mixed boryl silyl amines, the presence of silicon on nitrogen may lower the B—N bond order to some extent thereby increasing the B—O bond order. Thus in these derivatives, we tentatively assign to B—N and B—O stretching vibrations the bands in the region 1450 - 1500 cm^{-1} and 1300 - 1350 cm^{-1}, respectively.

Experimental

Bis(trimethylsilyl)amine was distilled before use. Tris(trimethylsilyl)amine [12], 2-chloro-1,3,2-dioxaborolane [13] and 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane [11] were prepared by published methods. The last compound, colourless when freshly distilled (b.p. 65°/0.5 mm), turns brown quickly. It was completely changed in a week at room temperature into a higher boiling liquid (b.p. 90°/0.5 mm) and a polymeric residue. No attempt was made to identify the distillate.

Reactions between bis(trimethylsilyl)amine and 2-chloro-1,3,2-dioxaborolane

1. An exothermic reaction occurred between 2-chloro-1,3,2-dioxaborolane (4.90 g, 1 mole) and bis(trimethylsilyl)amine (7.40 g, 1 mole) in benzene (25 ml). After refluxing the clear solution for 1 h, trimethylchlorosilane and benzene were distilled off. The residue (7.35 g) was distilled under reduced pressure to give 2-(trimethylsilylamino)-1,3,2-dioxaborolane (5.8 g, 78%), b,p. 33° (0.2 mm) as a colourless liquid. PMR spectrum, $\tau(CCl_4)$: $(CH_3)_3Si$, 9.90; CH_2, 5.95. (Found: B, 6.8; N, 8.7. $C_5H_{14}BNO_2Si$ calcd.: B, 6.8; N, 8.8%.)

2. An insoluble white solid was obtained with evolution of heat on mixing 2-chloro-1,3,2-dioxaborolane (5.60 g, 2 mole) and bis(trimethylsilyl)amine (4.2 g, 1 mole) in benzene (25 ml). Trimethylchlorosilane and benzene were removed and the solid was dried in vacuo. It was insoluble in organic solvents and did not form a mull with Nujol. (Found: B, 14.5; N, 8.5; Cl, 4.0. $C_4H_9B_2NO_4$ calcd.: B, 13.8; N, 8.9; Cl, 0%.

Reactions between tris(trimethylsilyl)amine and 2-chloro-1,3,2-dioxaborolane

1. Heat was evolved on adding 2-chloro-1,3,2-dioxaborolane (2.13 g, 1 mole) to tris(trimethylsilyl)amine (4.67 g, 1 mole). The liberated trimethylchlorosilane was removed under reduced pressure and the residue (4.6 g) on distillation afforded (1,3,2-dioxaborolan-2-yl)bis(trimethylsilyl)amine (3.8 g, 83%) as a colourless liquid, b.p. 65° (0.2 mm). PMR spectrum, $\tau(CCl_4)$: $(CH_3)_3Si$, 9.8; CH_2, 6.0 (Found: B, 4.6; N, 5.9. $C_8H_{22}BNO_2Si_2$ calcd.: B, 4.7; N, 6.1%.)

2. A mixture of 2-chloro-1,3,2-dioxaborolane (6.38 g, 2 mole) and tris(trimethylsilyl)amine (7.00 g, 1 mole) was kept at room temperature for 1 h. The liberated trimethylchlorosilane was removed in vacuo. The residue (10.2 g) was heated for 2 h at 130 - 140° and the liberated Me_3SiCl was again removed in vacuo. The process was repeated until no Me_3SiCl was formed. Finally, distillation under reduced pressure gave (trimethylsilyl)bis(1,3,2-dioxaborolan-2-yl)amine (4.5 g, 65%) as a colourless mobile liquid at 70° (0.05 mm). PMR spectrum, $\tau(CCl_4)$: $(CH_3)_3Si$, 9.8; CH_2, 5.9. (Found: B, 9.2; N, 5.8. $C_7H_{17}B_2NO_4Si$ calcd.: B, 9.4; N, 6.1%.)

3. Trimethylchlorosilane was removed repeatedly as in the previous experiment from a mixture of tris(trimethylsilyl)amine (7.4 g, 1 mole) and 2-chloro-1,3,2-dioxaborolane (16.0 g, 4.8 mole). Finally the residue (13.0 g) was distilled under reduced pressure. A colourless liquid (3.5 g) was obtained at 65 - 70° (0.2 - 0.25 mm). (Found: B, 7.8. $C_4H_8BClO_3$ calcd.: B, 7.7%.) A colourless polymeric solid residue (9.1 g) remained undistilled.

Reactions between bis(trimethylsilyl)amine and 2-chloro-4,4,6-trimethyl-1,3,2-dioxaborinane

1. A mixture of bis(trimethylsilyl)amine (3.2 g, 1 mole) and the chloroborinane (3.3 g, 1 mole) was stirred for 1 h and the liberated trimethylchlorosilane was removed in vacuo. Finally 2-(trimethylsilylamino)-4,4,6-trimethyl-1,3,2-dioxaborinane (3.9 g, 90%) was obtained at 60° (1 mm). PMR spectrum, $\tau(CCl_4)$; $(CH_3)_3Si$, 9.93 (singlet); $(CH_3)_2$, 8.8 (singlet); CH_2, 8.1 - 8.7 (multiplet); tertiary H, 5.9 (multiplet); CH_3, 8.85 (doublet). (Found: B, 4.9; N, 6.3. $C_9H_{22}BNO_2Si$ calcd.: B, 5.0; N, 6.5%.)

2. Removal of trimethylchlorosilane from a mixture of bis(trimethylsilyl)amine (2.7 g, 1 mole) and the chloroborinane (5.5 g, 2 mole) and distillation of the residue gave 2-(trimethylsilylamino)-4,4,6-trimethyl-1,3,2-dioxaborolane (0.5 g), b.p. 60° (1.2 mm) (authentic IR spectrum), a middle fraction (0.52 g), b.p. 60° (1.2 mm) to 119° (1.6 mm), bis(4,4,6-trimethyl-1,3,2-dioxaborolan-2-yl)amine (2.26 g, 50%), b.p. 120 - 125° (1.6 mm). (Found: B, 7.9; N, 5.0. $C_{12}H_{25}B_2NO_4$ calcd.: B, 8.0; N, 5.2%.) and an undistilled residue (1.26 g).

Acknowledgements

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