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GERMOBOROXANES

I. SYNTHESIS OF 2-(TRIBUTYLGERMYLOXY)-1,3,2-DIOXABOROLANES AND RELATED COMPOUNDS

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SUMMARY

Tris(tri-n-butylgermyl) borate and a number of 2-(tributylgermyloxy)-1,3,2-dioxaborole, -borolanes, and -borinanes have been prepared by several routes.

INTRODUCTION

Metallosiloxanes[1,2] (including borosiloxanes)[3] have been studied extensively during the last decade. In recent years, attention has been directed to other heterometalloxanes, *e.g.*, stannoboroxanes have been described recently[4]. In this paper, we report the synthesis of the first germoboroxanes.

RESULTS

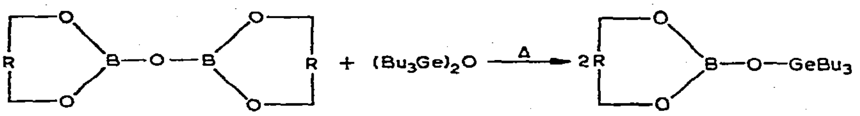
Tris(tri-n-butylgermyl) borate was obtained as a colourless distillable liquid by the azeotropic removal of water from a mixture of boric acid and bis(tri-n-butylgermanium) oxide:

$$2\,B(OH)_3 + 3\,(Bu_3Ge)_2O \rightarrow 2\,(Bu_3GeO)_3B + 3\,H_2O\uparrow \qquad (1)$$

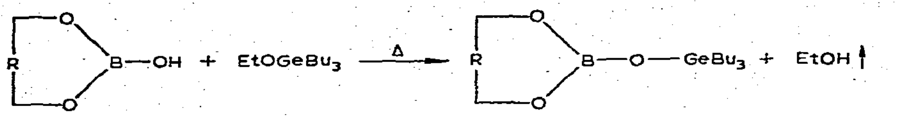
The progress of this reaction was followed by observing the disappearance of the strong and broad Ge–O–Ge peak[5] at 841 cm^{-1}.

2-(Tributylgermyloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane (IA) has been prepared similarly from boric acid, bis(tri-n-butylgermanium) oxide and the diol as well as by five other routes (3–7):

(2)



(3)



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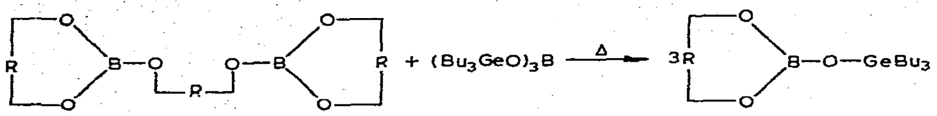

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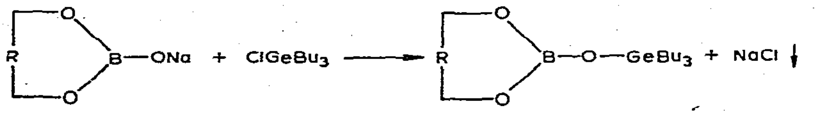
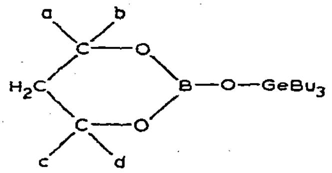


(6)

(7)

Reactions (3) and (5) show ready interchangeability of germyloxy and boryloxy groups. Reactions of the type (6) have previously been used to prepare alkylgermosiloxanes from alkali trialkylsilanolates and alkylhalogermanes[6].

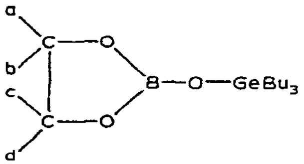
Reaction (2) has been utilised to prepare a variety of 2-(tributylgermyloxy)-1,3,2-dioxaborinanes (I), -borolanes (II) and -borole (III) in quantitative yields.



(I)

(A) a, b, c = Me ; d = H

(B) a, b, c, d = H

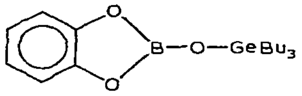


(II)

(A) a, b, c, d = Me

(B) a, b, c = H ; d = Me

(C) a, b, c, d = H



(III)

The reactions require longer times for completion than the analogous reactions used for the synthesis of the corresponding tributylstannoxy derivatives[4].

Compounds (I–III) are colourless distillable liquids, and do not show any tendency to disproportionate into the symmetrical metalloxanes. They are monomeric, and appear to be hydrolytically more stable than the corresponding tributylstannoxy derivatives.

Infrared spectra

The spectrum of tris(tri-n-butylgermyl) borate shows a very strong band at 1310 cm^{-1}, which may be assigned to the B–O–Ge asymmetric stretch [*cf.* B–O–C at 1342 cm^{-1} in $B(OCMe_3)_3$[7]; B–O–Si at 1333 cm^{-1} in $B(OSiMe_3)_3$[8] and B–O–Sn at 1290–1275 cm^{-1} in $B(OSnBu_3)_3$[4]].

2-(Tributylgermyloxy)-1,3,2-dioxaborolanes and -borinanes show ν_{as}(B–O–C) in the region 1470–1380 cm^{-1} and ν_{as}(B–O–Ge) at 1290 ± 10 cm^{-1} [(IA) 1380, 1360 vs and 1295 cm^{-1} vs (br); (IB) 1405, 1350 cm^{-1} vs and 1285 cm^{-1} vs; (IIA) 1425 vs (br) and 1280 cm^{-1} vs (br); (IIB) 1461–1441 vs (br) and 1295 cm^{-1} s (br); (IIC) 1400 vs, 1350 vs and 1280 cm^{-1} vs (br)].

In compound (III), ν_{as}[B–O–C (aromatic)] appears as a strong band at 1450 cm^{-1}, and appears in the same range as in other 2-substituted 1,3,2-benzodioxaborole[9] and related derivatives.

In the lower frequency region, there is a very strong and broad peak at 1238 cm^{-1}, which may be due to ν_{as}(B–O–Ge) and ν_{as}(C–O).

EXPERIMENTAL

All the glycols and bis(tri-n-butylgermanium) oxide were distilled before use. Ethoxytri-n-butylgermane was prepared by the ammonia method[10]. Molecular weights were determined in benzene solution by osmometry.

Boron was estimated as boric acid by hydrolysing the sample in hot water. The carbon and hydrogen analysis were carried out by the Australian Microanalytical Service, CSIRO, Melbourne, Australia.

(1). *Reaction of bis(tri-n-butylgermanium) oxide with boric acid in the molar ratio 3/2*

Azeotropic removal of water from a mixture of bis(tri-n-butylgermanium) oxide (2.5 g), boric acid (0.21 g) and benzene (≈60 ml) gave tris(tri-n-butylgermyl) borate (2.54 g; 97% yield), b.p. 193/0.6 mm. The reaction is completed within 12 h. (Found: C, 55.1; H, 10.6; B, 1.4. $C_{36}H_{81}BGe_3O_3$ calcd.: C, 54.7; H, 10.3; B, 1.4%.)

(2). *Reaction of bis(tri-n-butylgermanium) oxide with 2-methyl-2,4-pentanediol and boric acid in the molar ratio 1/2/2*

A mixture of bis(tri-n-butylgermanium) oxide (1.67 g), boric acid (0.4 g) and

TABLE 1

$(Bu_3Ge)_2O$ (g)	*Glycol (g)*	*Boric acid (g)*	*Yield (%)*	*B.p. (°C/mm)*	*n_D^{20}*	*Analysis Found (calcd.)*		
						B	*C*	*H*
1.67	2-Methyl-2,4-pentanediol (0.78)	0.40	66	122/0.6	1.4430	2.9 (2.8)	56.3 (55.9)	10.2 (10.2)
1.89	2,3-Dimethyl-2,3-butanediol (0.89)	0.50	77	115/0.6	1.4425	2.8 (2.8)	56.6 (55.9)	10.5 (10.2)
2.96	1,2-Ethanediol (0.72)	0.73	96	119/0.9	1.4580	3.2 (3.3)	50.2 (50.8)	9.4 (9.5)
2.60	1,2-Propanediol (0.78)	0.66	70	109/0.7	1.4475	3.0 (3.1)	52.4 (52.1)	9.9 (9.6)
2.02	1,3-Propanediol (0.62)	0.50	74	124/0.7	1.4545	3.0 (3.1)	52.2 (52.3)	9.8 (9.6)
2.82	1,2-Benzenediol (1.23)	0.70	93	142/0.7	1.4890	2.9 (2.9)	57.3 (57.1)	8.4 (8.3)

the diol (0.78 g) in benzene (≈60 ml) was refluxed for about 4 h with simultaneous removal of water. Distillation at 122°/0.6 mm gave a colourless liquid (1.68 g; 66% yield).

The compounds, prepared similarly from other diols, are listed in Table 1.

(3). *Reaction of bis(tri-n-butylgermanium) oxide with 2,2′-oxy(bis-4,4,6-trimethyl-1,3,2-dioxaborinane) in the molar ratio* 1/1

On heating a mixture of the oxybis(dioxaborinane) (0.68 g) and bis(tri-n-butylgermanium) oxide (1.28 g) for about 4 h and on distillation of the resulting product at 0.8 mm, a colourless liquid (1.8 g; 97% yield) was obtained at 132–134° (authentic IR spectrum).

(4). *Reaction of 2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane with ethoxytri-n-butylgermane in the molar ratio* 1/1

Condensation of ethoxytri-n-butylgermane (2.58 g) with 2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane (1.27 g) *in vacuo* for about 2 h at 80°/5 mm yielded (IA) (authentic IR spectrum), b.p. 112°/0.4 mm (2.8 g; 81% yield).

(5). *Reaction of 2,2′-(1,1,3-trimethyltrimethylenedioxy)bis(4,4,6-trimethyl-1,3,2-dioxaborinane) with tris(tri-n-butylgermyl) borate in molar ratio* 1/1

A mixture of tris(tri-n-butylgermyl) borate (0.51 g) and 2,2′-(1,1,3-trimethyltrimethylenedioxy)bis(4,4,6-trimethyl-1,3,2-dioxaborinane (0.24 g) was heated for about 12 h. On distillation of the resulting product, a colourless liquid (b.p. 108–9°/0.5 mm) was obtained (authentic IR spectrum).

(6). *Reaction of sodium salt of 2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane with tri-n-butylchlorogermane in the molar ratio* 1/1

Removing sodium chloride from a mixture of sodium salt (2.4 g), tri-n-butylchlorogermane (3.6 g) and benzene (≈30 ml) after refluxing for 11 h gave a colourless solution which on distillation yielded a liquid at 130–132°/0.8 mm (3.4 g; 69% yield; authentic IR spectrum).

(7). *Reaction of tri-n-butylchlorogermane with 2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane in presence of triethylamine in the molar ratio* 1/1

A mixture of tri-n-butylchlorogermane (2.24 g), 2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane (1.16 g), triethylamine (1.2 g) and benzene (50 ml) was heated for about 3 h. After removing triethylamine hydrochloride (0.96 g), by filtration, (IA) was distilled at 105–108°/0.4 mm (2.1 g; 76% yield). (Found: B, 3.0. $C_{18}H_{39}BGeO_3$ calcd.: B, 2.8%.)

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