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METAL DERIVATIVES OF AMIDOXIMES

II. SYNTHESIS OF 2-(TRIBUTYLSTANNOXY)-, 2-(TRIPHENYLSTANNOXY)-AND 2-(TRIMETHYLSILOXY)-3-HYDRO-4-ALKYL OR -4-PHENYL-1,3,5,2-OXADIAZABOROLES

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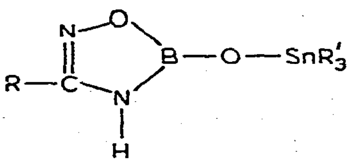
Summary

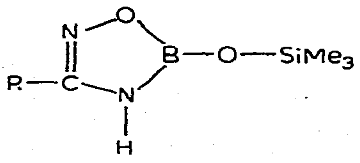
2-(Tributylstannoxy)-, 2(triphenylstannoxy)- and 2-(trimethylsiloxy)-3-hydro-4-alkyl- or -4-phenyl-1,3,5,2-oxadiazaboroles have been synthesized, and their properties examined.

Introduction

Industrial applications of siloxane polymers have led to the development of the chemistry of heterometalloxanes containing M—O—M′ bonds [1]. Metalloboroxanes containing M—O—B bonds have also received considerable attention, but stannoboroxanes (compounds with Sn—O—B bonds) and borosiloxanes (compounds with Si—O—B bonds) have been little studied [2, 3]. In earlier reports [4—6] we described the boron and silicon derivatives of amidoximes. In this paper we report the synthesis of some 2-(tributyl- or triphenyl-stannoxy)- (Ia, Ib) and 2-(trimethylsiloxy)- (II) -3-hydro-4-alkyl- or -4-phenyl-1,3,5,2-oxadiazaboroles.



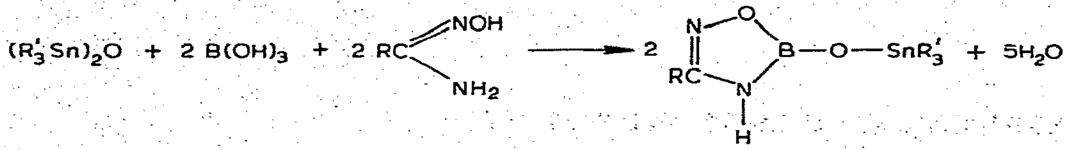
(I) a, R′ = Bu ;
b, R′ = Ph



(II)

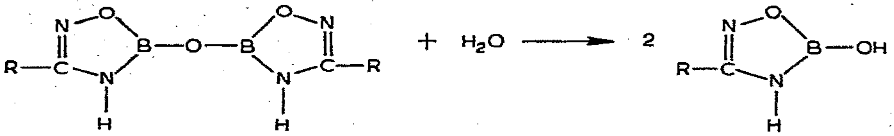
(R = Me, Et, Pr or Ph)

Compounds Ia and Ib were obtained by azeotropic removal of water with benzene from a mixture of bis(tributyltin) or bis(triphenyltin) oxide, boric acid and the appropriate amidoxime in 1/2/2 molar ratio:

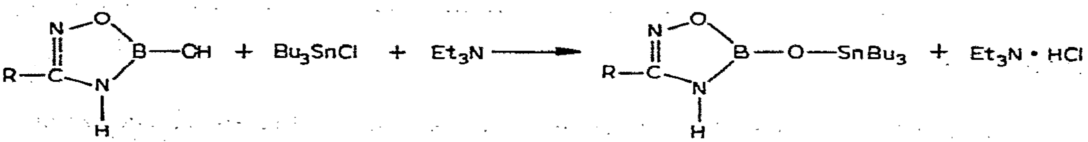


(R′ = Bu or Ph).

The completion of the reaction is indicated by the complete disappearance of the strong Sn—O—Sn peak at ≈ 770 cm^{-1} in the infrared spectrum of the reaction mixture. The yields were quantitative in every case. Products Ia have also been synthesized by the controlled hydrolysis of 2,2′-oxybis(3-hydro-4-alkyl- or -4-phenyl-1,3,5,2-oxadiazaborole) (III) [6] followed by reaction with tributyltin chloride in the presence of triethylamine as hydrogen chloride acceptor:

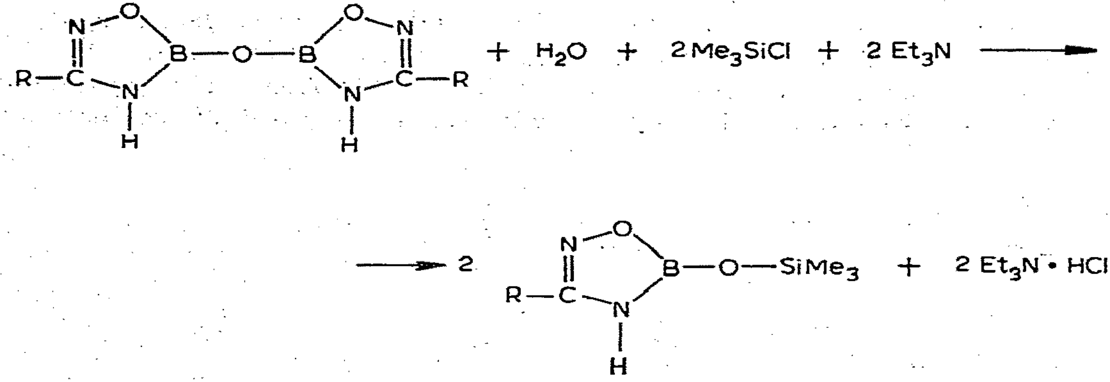


(III)



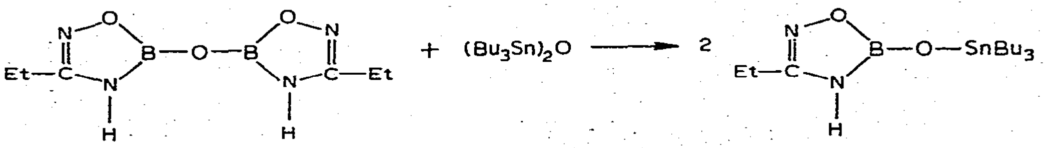
(Ia)

Compounds II were obtained similarly from trimethylchlorosilane:

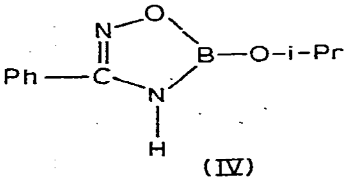


(II)

The boroxy and stannoxy groups have a tendency to interchange, as demonstrated by the following reaction:



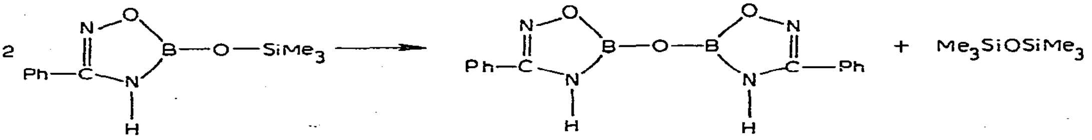
Preparation of II was also attempted by the reaction of trimethylsilyl acetate with 2-isopropoxy-3-hydro-4-phenyl-1,3,5,2-oxadiazaborole (IV), [6] in cyclohexane. The reaction was extremely slow and did not reach to completion even when refluxed for longer time.



(IV)

Compounds Ia are colourless volatile viscous liquids, except for 2-(tributylstannoxy)-3-hydro-4-methyl-1,3,5,2-oxadiazaborole, which is a white solid (Table 1). Compounds Ib are white sublimable solids. Compounds II are volatile colourless liquids or very low melting solids. All compounds Ia, Ib and II are monomeric in benzene.

The product 2-(trimethylsiloxy)-3-hydro-4-phenyl-1,3,5,2-oxadiazaborole could be distilled in about 45% yield, but did at the same time undergo decomposition:



Infrared spectra

The main features are:

(i). In compounds I and II, the absence of two strong bands in the range 3570—3650 and 3450—3487 cm^{-1} present in the amidoxime due to $\nu(OH)$ and $\nu(NH_2)$ respectively indicate deprotonation.

(ii). The presence of two strong bands in the range 3320—3360 and 3150—3200 cm^{-1} (slightly broader in nature) suggests the presence of free and hydrogen bonded $\nu(NH)$, respectively. The >NH deformation can also be seen as a weak peak at $\approx$ 1580 cm^{-1}.

(iii). An intesne band appears in the range 1630—1660 cm^{-1} and is due to $\nu(C{=}N)$.

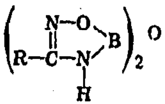
(iv). Stretching vibrations due to B—N in the products appear in the region 1360—1390 cm^{-1} [7].

(v). Compounds II are characterised by an intense band at 1330 ± 10 cm^{-1} due to ν(B—O) of B—O—N and B—O—Si [8].

(vi). Compounds Ia and Ib show two types of ν_{as}(B—O) peaks in the regions

TABLE 1. PREPARATIONS AND ANALYSES OF SOME NEW STANNOBOROXANES AND BOROSILOXANES

S. No.	*Preparative method 1* [a] Bis-(tributyltin) or -(triphenyltin) oxide	Amidoxime $RC(=NOH)NH_2$	Boric acid (g)	Yield (%)	B.p. (°C/mmHg)	Analysis found (calcd.) (%) B	Sn or Si	N
	$(Bu_3Sn)_2O$						*Sn*	
1	3.05	R(g) = Me(0.76)	0.63	46	160—165/0.4 [b]	2.74 (2.78)	30.36 (30.55)	7.08 (7.20)
2	3.05	Et(0.90)	0.63	90	88—90 /0.1	2.62 (2.68)	29.35 (29.49)	6.82 (6.96)
3	3.05	Pr(1.05)	0.63	90	91—92 /0.1	2.54 (2.60)	28.26 (28.49)	6.65 (6.73)
4	4.21	Ph(1.93)	0.87	40	118—120/0.1	2.32 (2.40)	26.28 (26.34)	6.13 (6.22)
	$(Ph_3Sn)_2O$							
5	2.13	Me(0.44)	0.37	42	160—170/0.1 [b]	2.42 (2.41)	26.30 (26.44)	6.01 (6.24)
6	4.24	Et(1.04)	0.73	43	200—210/0.4 [b]	2.31 (2.34)	25.24 (25.65)	5.96 (6.05)
7	1.76	Pr(0.50)	0.30	50	200—210/0.4 [b]	2.18 (2.27)	24.70 (24.89)	5.76 (5.87)
8	3.26	Ph(1.24)	0.56	40	210—220/0.1 [b]	2.05 (2.12)	23.01 (23.24)	5.48 (5.48)

S. No.	*Preparative method 2*	H_2O (g)	Et_3N (g)	Me_3SiCl (g)	Yield (%)	B.p. (°C/mmHg)	B	Si	N
									
9	R(g) = Me(1.14)	0.11	1.26	1.34	75	56—58 /0.5	6.18 (6.29)	16.15 (16.35)	16.18 (16.31)
10	Et(1.71)	0.15	1.68	1.77	75	68—70 /0.6	5.70 (5.84)	14.82 (15.18)	14.99 (15.14)
11	Pr(2.14)	0.16	1.85	1.94	85	65—66 /0.3	5.35 (5.43)	14.00 (14.10)	13.99 (14.07)
12	Ph(4.88)	0.29	3.30	3.55	45 [c]	113—115/0.1	4.59 (4.63)	11.86 (12.03)	11.82 (12.00)

[a] Compounds 1—4 have also been synthesized by preparative method 2. Yield (40—50%) of products 1, 4—8 is due to decomposition into $(R_3Sn)_2O$. [b] Sublimation temp. [c] *(i)* A colourless liquid (0.65 g; b.p. 98.5°) was trapped and its IR corresponded to $(Me_3Si)_2O$; *(ii)* A residue (1.20 g) was left (found: B, 7.19; N, 18.43. $C_{14}H_{12}B_2O_3N_4$ calcd.: B, 7.23; N, 18.72%.)

1330—1380 and 1275—1285 cm^{-1}; the former may be due to B—O—N and the latter to B—O—Sn [9].

(vii). The trimethylsilyl group gives typical characteristic absorption bands of three methyls on silicon at ≈ 760 and 840—845 cm^{-1}, due to methyl rocking [10], along with the $\delta_s(CH_3)$ band at ≈ 1250 cm^{-1} in the products II.

(viii). There is a medium band at ≈ 920 cm^{-1}, assignable to the N—O vibration.

Experimental

Special precautions were taken to exclude moisture. Tetrahydrofuran, benzene and triethylamine were dried [4]. Freshly distilled trimethylchlorosilane (57.7°), bis(tributyltin) oxide (b.p. 150—157/0.05 mm) and freshly prepared bis(triphenyltin) oxide (m.p. 119—120°) were used. Amidoximes were prepared by standard methods [11, 12].

Analytical methods

Boron was determined by hydrolysing the compound with 80% ethanol and titrating the boric acid produced against standard sodium hydroxide solution in the presence of mannitol, with phenolphthalein as indicator. Tin was determined as tin oxide by decomposing the compound with fuming nitric and sulphuric acids, and precipitating tin hydroxide by addition of ammonium hydroxide, ammonium nitrate (≈ 30 g) being added to avoid coagulation. Silicon was determined as silica [13] and nitrogen by the Kjeldahl method.

Molecular weights were determined ebullioscopically in boiling benzene with a semimicro ebulliometer employing thermistor sensing. IR spectra were recorded on a Perkin—Elmer-337 instrument in the range of 4000—400 cm^{-1}, neat or in Nujol, using KBr plates.

(1). Reaction between bis(tributyltin) oxide, boric acid and amidoxime in 1/2/2 molar ratio

Azeotropic removal of water with benzene (≈ 65 ml) from a mixture of bis(tributyltin) oxide, boric acid and amidoxime gave a product volatile under reduced pressure.

2-(Triphenylstannoxy)-3-hydro-4-alkyl- or -4-phenyl-1,3,5,2-oxadiazaboroles were synthesized similarly. Results are shown in Table 1.

(2). Reaction of 2,2'-oxybis(3-hydro-4-alkyl- or -4-phenyl-1,3,5,2-oxadiazaborole with tributyltin chloride (or trimethylchlorosilane) in the presence of triethylamine (molar ratio 1/2/2)

To 2,2'-oxybis(3-hydro-4-alkyl- or -4-phenyl-1,3,5,2-oxadiazaborole in THF (40 ml), water was added in stoichiometric proportion. The mixture was stirred for ≈ 10 h. Triethylamine was added, followed by tributyltin chloride or trimethylchlorosilane, and the system was stirred and refluxed. The solid was filtered off, and the volatile material evaporated off to give a distillable or sublimable product (Table 1).

(3). Reaction between 2,2'-oxybis(3-hydro-4-ethyl-1,3,5,2-oxadiazaborole) and bis(tributyltin) oxide in 1/1 molar ratio

Heating a mixture of bis(tributyltin) oxide (4.25 g) and 2,2'-oxybis(3-hydro-4-ethyl-1,3,5,2-oxadiazaborole) (1.49 g) and distilling under reduced pressure, gave a colourless viscous compound (93% yield), b.p. 88—90°/0.1 mm. (Found: B, 2.58; N, 6.89; Sn, 29.24. $C_{15}H_{33}BN_2O_2Sn$ calcd.: B, 2.68; N, 6.96; Sn, 29.49%.)

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