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Metal Derivatives of Amidoximes. VII. Synthesis of Bis(1,3,5,2-Oxadiazaborol-2-yloxy)tetrabutyldistannoxanes

A. B. Goel and V. D. Gupta
Chemistry Department, Rajasthan University, Jaipur-302004, India

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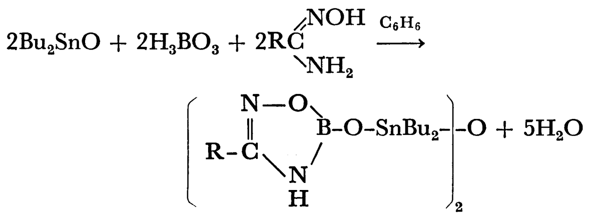
Synopsis. Bis(1,3,5,2-oxadiazaborol-2-yloxy)tetrabutyldistannoxanes have been synthesized by the reaction of amidoxime, boric acid and dibutyltin oxide. A probable structure for the dimeric species has been proposed on the basis of molecular weight and IR spectral data.

Industrial importance of polymers like silicones[1] has given impetus to the study of metalloboroxanes containing B-O-M linkage.[2] In continuation to our earlier report[3] we briefly communicate here the synthesis and characterization of the dibutylstannoxy boron derivatives containing amidoxime ring.

Bis(1,3,5,2-oxadiazaborol-2-yloxy)tetrabutyldistannoxanes (I) have been synthesized from the mixture of dibutyltin oxide, boric acid and amidoxime by removing water azeotropically with benzene.



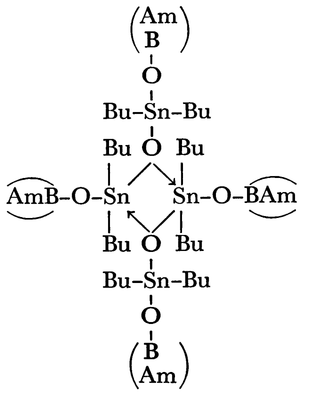
(I)

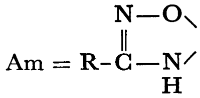
(R=Me, Et, Pr or Ph)

The reactivity of dibutyltin oxide with amidoxime[4] and boric acid[5] in refluxing benzene indicates that probably amidoxime reacts preferentially with boric acid with the formation of $[R(HN)C{=}N{-}OB{-}]_2{-}O$ (II) which with dibutyltin oxide gives the final product (I). This has been substantiated by the interchange reaction of II[6] with dibutyltin oxide which furnishes I.

These products are white crystalline solids re-crystallizable from hot benzene and are dimeric in refluxing benzene as revealed by molecular weight data.

Infrared spectrum of I shows the characteristic bands[7] due to νNH in the region 3250—3350 cm^{-1}, νC=N at 1646±5 cm^{-1} and νN–O at 920±10 cm^{-1}. Bands at 1275±5 and 1240±10 cm^{-1} due to νB–O (–Sn) and at 595 and 565±5 cm^{-1} due to ν(Sn–O–Sn) indicate the possibility of ladder type structure[8] for these products (I).





The more detailed structural work is in progress.

Experimental

Dibutyltin oxide (Nitto Kasei) and boric acid were used as supplied. Amidoximes were prepared by standard methods.[9] Boron, tin and nitrogen were estimated by the methods reported earlier.[3] Infrared spectra were recorded on Nujol on Perkin-Elmer 337 spectrophotometer in the range 4000—400 cm^{-1} using KBr optics. Molecular weights were determined on an ebulliometer (Gallenkamp).

Table 1. Preparation of $[R(NH)C{=}N{-}O{-}B{-}O{-}SnBu_2{-}]_2{-}O$ (I)

Reactants (mmol)			Refluxed for (hr)	Yield (%)	Product (I) (mp °C) R=	Analysis(%) Found(Calcd)			Mol. wt. Found (Calcd)
$R(NH_2)C{=}NOH$ R=	Boric acid	Bu_2SnO				B	Sn	N	
Me 12.5	12.3	12.4	16	88	Me(155—158)	3.10 (3.18)	34.7 (34.9)	8.13 (8.24)	1405 (679.6)
Et 9.5	9.5	9.4	13	90	Et(150—157[a])	3.0 (3.06)	33.4 (33.50)	7.84 (7.93)	1438 (707.6)
Pr 9.3	9.4	9.4	12	85	Pr(110—115[a])	2.88 (2.94)	32.0 (32.3)	7.60 (7.62)	1506 (735.6)
Ph 12.7	12.7	12.8	10	92	Ph(90—92)	2.63 (2.69)	29.6 (29.5)	7.40 (7.47)	1587 (803.8)

a) With decomposition.

Reaction between Dibutyltin Oxide, Boric Acid and Amidoxime. Removal of water azeotropically with benzene (~60 ml) from an equimolar mixture of dibutyltin oxide, boric acid and amidoxime left a clear solution. After removing the solvent *in vacuo*, the product (I) is obtained as white solid recrystallizable from benzene. The details are given in Table 1.

Reaction between II(R=Ph) and Dibutyltin Oxide. A mixture of II,[6] R=Ph (0.98, 3.23 mmol) and dibutyltin oxide (1.61 g, 6.47 mmol) was refluxed in benzene (~40 ml) for about 9 hr leaving a clear solution. On removing excess benzene a white product (2.36 g, 90% yield, mp 90—92 °C) crystallized out. Found: B, 2.62; Sn, 29.5; N, 7.30%. Calcd for I (R=Ph), B, 2.69; Sn, 29.5; N, 7.47%.

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