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Seven membered ring chelates derived from γ-hydroxyamides and triphenyltin or diphenylboron

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ABSTRACT

N-Benzyl-4-hydroxy-butyramide (**1**), 4-hydroxy-*N*-[(R)-1-phenyl-ethyl]-butyramide (**2**), and (R)-4-hydroxy-2-methyl-*N*-[(R)-1-phenyl-ethyl]-butyramide (**3a**) were used to prepare new diphenylboron and triphenyltinoxy compounds: diphenylborinic acid 3-benzylcarbamoyl-propyl ester (**4**), diphenylborinic acid 3-[(R)-1-phenyl-ethylcarbamoyl]-propyl ester (**5**) and diphenylborinic acid (R)-3-[(R)-1-phenyl-ethylcarbamoyl]-butyl ester (**6**), N-benzyl-4-triphenyltinoxy-butyramide (**7**), 4-triphenyltinoxy-*N*-[(R)-1-phenyl-ethyl]-butyramide (**8**), and (R)-4-triphenyltinoxy-2-methyl-*N*-[(R)-1-phenyl-ethyl]-butyramide (**9**). The X-ray diffraction analysis of a crystalline structure of the new γ-hydroxyamide **3a** is reported, as well as that of the first example of a crystalline structure where a diphenylborinic ester forms a seven membered chelate, by a carbonyl coordination to boron (**4**). Structural studies of tin and boron esters were performed by NMR. The C=O internal coordination to tin atoms, affording seven membered rings, was observed by ^{119}Sn NMR experiments at low temperature.

1. Introduction

Interest in the structure and reactivity of proteins has motivated the investigation of amide group coordination to metal atoms [1]. In this context, γ-hydroxyamides are good candidates for formation of coordination compounds with triphenyltin or diphenylboron compounds because of their three potential reactive sites; the OH, N–H and carbonyl groups. γ-Hydroxyamides have important pharmacological activities, for example, as anticonvulsants [2,3], whereas tin compounds have biocidal properties [4–9], and boron derivatives have potential uses in cancer therapies [10–13].

Our interest in the structural investigation of γ-hydroxyamide derivatives is based on the fact that if the OH proton is substituted, the Lewis acid could be intramolecularly coordinated by the carbonyl group affording seven membered rings. Formation of five membered chelates by base coordination to boron and tin is common, whereas six membered chelates are less well known and seven membered rings are seldom reported [14]. The fact that seven membered chelates are weak could explain the lack of examples for triphenyltin esters formed by oxygen coordination and the few reported examples for boron chelates [15]. An $O \rightarrow BH_2O$ seven membered chelate was recently reported [16]. However, X-ray diffraction analyses for compounds forming seven membered rings by carbonyl coordination to boron are unknown. Where the possibility of seven membered chelates exists in tin compounds, for example in triphenyltin(IV) complexes of *N*,*N*′-disubstituted dihydroxamic acids [17], or of monomethyl phthalate [18], the formation of two five membered rings or a lineal arrangement is preferred, as in the case of μ-succinato-bis(aquatriphenyltin)-bis(o-phenanthroline) [19]. Of additional relevance to this study is the scarcity of reports of amide coordination to boron [20] or tin [21–23], probably due to the low energy of the coordination which results in less stable compounds.

Herein, we report the synthesis and characterization of diphenylborinic esters (**4**–**6**) and triphenyltin alkoxides (**7**–**9**) derived from γ-hydroxyamides (**1**–**3**), Scheme 1. As various coordination compounds derived from γ-hydroxyamides could be expected, depending on the reaction site and on their substitution, we decided to investigate the reactions with γ-hydroxyamides **1**–**3**, having different combination of methyl groups at C2 and/or at C5. Compounds **1** and **2** are known pharmaceuticals used for treatment of addiction and alcoholism [24–26]. Optically active (R)-4-hydroxy-2-methyl-*N*-[(R)-1-phenyl-ethyl]-butyramide (**3a**) is a new compound. Our interest is focused on the structural analyses of compounds **1**–**9**, in particular the evaluation of intramolecular hydrogen bonds ($O{-}H\cdots O{=}C$) and $O{-}Sn \leftarrow O{=}C$ or $O{-}B \leftarrow O{=}C$ internal coordination through seven membered ring formation.

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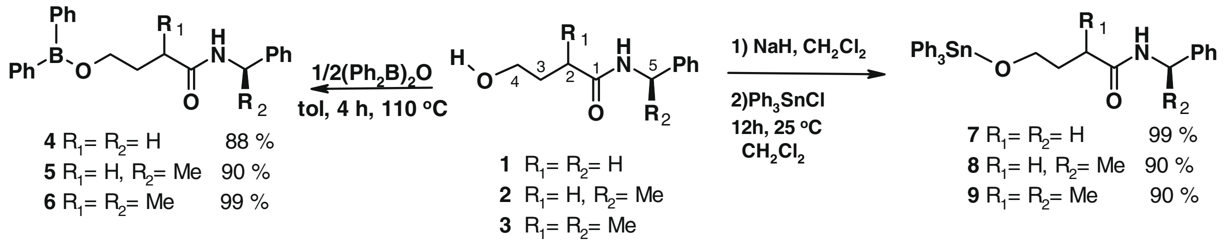


Scheme 1. Synthesis of boron (**4**–**6**) and tin (**7**–**9**) derivatives.

2. Results and discussion

2.1. Syntheses of γ-hydroxyamides 1–3

γ-Hydroxyamides **1**–**2** were prepared with good yields by aminolysis of γ-butyrolactone using benzylamine and optically active (R)-2-methylbenzylamine, respectively. The reaction of (±)-2-methyl-γ-butyrolactone with (R)-2-methylbenzylamine afforded two diasteromers: **3a** (2R,5R) and **3b** (2S,5R), Scheme 2. Compound **3a** was isolated pure by crystallization from DMSO and its structure was obtained by X-ray diffraction analysis. However, we were unable to isolate its pure epimer (**3b**), and only its NMR data was recorded.

The ^{1}H NMR spectrum of compound **1** shows the methylene groups as triplets indicating free rotation of C–C bonds. For compounds **2** and **3**, the AB coupling system for CH_2-3 is attributed to their stereogenic centers. The values of the coupling constant $^3J(^1H–^1H) \approx 6.3–7.2$ Hz of H5 with N–H measured for some of the compounds (**2**, **3**, **6** and **9**), indicate that the N–C5 bond rotation is already anchored and that the protons are in *anti* position, as was confirmed by the fact that NMR experiments at low temperature did not produce relevant changes in the chemical shifts of **1**–**3**. ^{15}N NMR of data of **1**–**3** is characteristic of NH amides. The methyl groups shift the ^{15}N signals of **2** and **3** to lower frequencies with respect to **1** (Δδ 12–14 ppm), Table 1.

2.1.1. Solid state study of compound 3a

The X-ray diffraction analysis of compound **3a** shows that atoms C7, N6, C1, O15 and C2 are in the same plane, with the ethanol and phenyl groups on one side of this plane. It is noteworthy that the O–H proton is not internally coordinated to the C=O, (Fig. 1). Instead, the carbonyl oxygen atom presents three intramolecular weak C–H hydrogen bonds forming five membered rings (O15···H7, 2.57; O15···H143, 2.90; and O15···H31, 2.56 Å), (Fig. 2). The highest distance incidence for contacts C–H···O has been estimated as being around 2.7 Å [27], however distances as longer as 3.0 Å have been reported. Intermolecular strong hydrogen bonds are formed between N–H···O (2.11 Å) and O–H···O (1.88 Å) giving polymeric arrangements, (Fig. 3).

Table 1
^{119}Sn and ^{15}N NMR data of **7**–**9** (CD_2Cl_2).

Compound	^{15}N (+25 °C)	Compound	^{15}N (+25 °C)	^{11}B (+25 °C)
1	−259.4[92.1]	**4**	−260.1[92.9]	+44.2
2	−245.0[92.1]	**5**	−246.3 [91.8]	+43.4
3a	−246.6[92.1]	**6**	−240.9	+45.0
3b	−247.0[91.1]			
Compound	^{15}N (+25 °C)	^{119}Sn (+25 °C)	^{119}Sn (−70 °C)	^1J(C*i*-Sn)
7	−257.8	−68.4	−110	not obs.
8	−246.0	−98.5	−210	630.0
9	−247.9	−63.6	−140	622.7

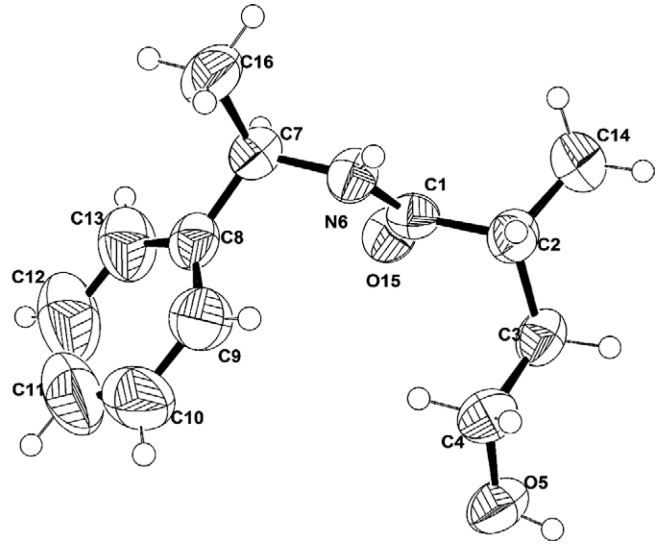
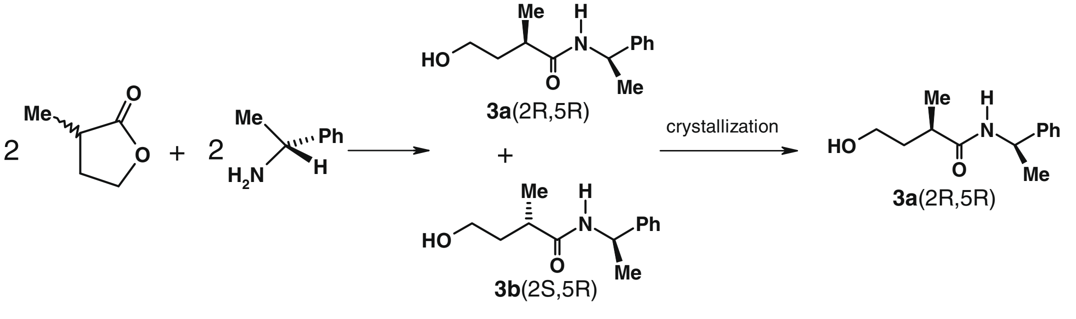


Fig. 1. ORTEP representation of compound **3a**.

2.2. Syntheses of diphenylborinic esters 4–6

Diphenylborinic esters **4**–**6** were prepared in good yields (88–99%) by condensation reactions of γ-hydroxyamides **1**, **2** and **3a**



Scheme 2. Synthesis of compound **3a**.