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Formation of a Pentacoordinate 1,2-Oxastannetanide by Novel Base-Induced Rearrangement of a Bis(β-Hydroxyalkyl)Stannane

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FORMATION OF A PENTACOORDINATE 1,2-OXASTANNETANIDE BY NOVEL BASE-INDUCED REARRANGEMENT OF A BIS(β-HYDROXYALKYL)STANNANE

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Treatment of a bis(β -hydroxyalkyl)diphenylstannane with potassium hydride in THF in the presence of 18-crown-6 gave the corresponding pentacoordinate *t*-alkoxy-1,2-oxastannetanide as stable crystals instead of a hexacoordinate stannate with two oxetane rings. This compound is considered to be formed by novel tin-1,3-migration reaction from carbon to oxygen reaction involving the formation of an oxetane ring and the subsequent tin-carbon bond cleavage.

<u>Keywords</u>: oxastannetane, tin-Peterson reaction, pentacoordinate stannate, homo-Brook type rearrangement, $bis(\beta-hydroxyalkyl)$ stannane

INTRODUCTION

In the course of our study on heteracyclobutanes bearing highly coordinate main group elements at the position adjacent to the heteroatom^[1], we have reported the syntheses and isolation of $1^{[2]}$, $2^{[3]}$ and $3^{[4]}$, which are the intermediates of the Wittig, the Peterson, and the Sn-Peterson reactions, respectively. We have also found that spirobi[1,2-oxaphosphetane]s $4^{[5]}$ show interesting reactivity, namely double olefin extrusion when the substituents at the 4-position was appropriate. During the attempted synthesis of hexacoordinate stannate 5 with two oxastannetane rings we have found the formation of a

pentacoordinate stannetanide by novel base-induced rearrangement of a $bis(\beta-hydroxyalkyl)$ stannane.



RESULTS AND DISCUSSION

Synthesis of bis(\beta-hydroxyalkyl)stannane

Bis(β -hydroxyalkyl)stannane 7 as a key intermediate was synthesized Bis(butyltelluromethyl)stannane 6 was preas shown in Scheme 1. pared in 53% yield by the reaction of dichlorodiphenylstannane with 2 equiv. of butyltelluromethyllithium in THF, which was generated in situ by treatment of bis(butyltelluro)methane with *n*-BuLi according to the The reaction of bis(lithiomethyl)stannane^[7], which was literature^[6]. generated by the treatment of 6 with 2.2 equiv. of *n*-BuLi, with hexafluoroacetone. followed by NH₄Cl gave bis(Baq. hydroxyalkyl)stannane 7 in 21% yield.

$$Ph_{2}SnCl_{2} \xrightarrow{2 BuTeCH_{2}Li} Ph_{2}Sn(CH_{2}TeBu)_{2} \xrightarrow{3)} H_{3}O^{+} Ph_{2}O^{+} Ph_{2}O^{+} Ph_{2}O^{+} Ph_{2}O^{+} Ph_{3}O^{+} Ph_{4}O^{+} CF_{3}O^{+} Ph_{4}O^{+} P$$

Reaction of $bis(\beta$ -hydroxyalkyl)stannane with potassium hydride

The reaction of 7 with potassium hydride in THF in the presence of 18crown-6 was monitored by ¹⁹F and ¹¹⁹Sn NMR spectroscopy at room temperature. Just after the addition of potassium hydride, the reaction mixture showed a signal at δ_{sn} –148.4 in ¹¹⁹Sn NMR, which is attributed to the bis(β -oxidoalkyl)stannane 8, in place of that of the starting material 7 (δ_{sn} –103.2). After 2 days 8 was completely disappeared, and pentacoordinate 1,2-oxastannetanide 9 was formed in 88% yield instead of the corresponding hexacoordinate spirobi[1,2oxastannetanide] 5. The ¹¹⁹Sn chemical shift of 9 is δ_{sn} –246.4, which is a reasonable value as the pentacoordinate tin compound^[4]. ¹H, ¹³C and ¹⁹F NMR data also supported this structure.



This compound is considered to be formed by novel tin-1,3migration reaction from carbon to oxygen^[8] involving the formation of oxetane ring and the subsequent Sn-C bond cleavage. This reactivity remarkably contrasts with that of **3**, which gave the corresponding olefin quantitatively^[4]. This base-induced migration reaction of **7** may proceed via a hexacoordinate tin species, although a proton source of this reaction have been not determined yet.

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