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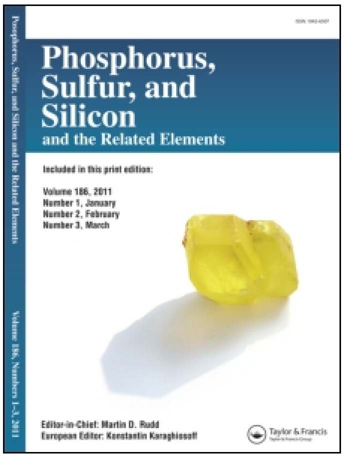

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FORMATION OF A PENTACOORDINATE 1,2-OXASTANNETANIDE BY NOVEL BASE-INDUCED REARRANGEMENT OF A BIS(β-HYDROXYALKYL)STANNANE

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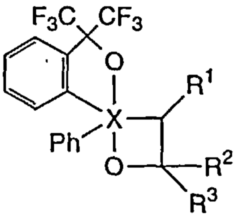
Treatment of a bis(β-hydroxyalkyl)diphenylstannane with potassium hydride in THF in the presence of 18-crown-6 gave the corresponding pentacoordinate *t*-alkoxy-1,2-oxastannetanide as stable crystals instead of a hexacoordinate stannate with two oxetane rings. This compound is considered to be formed 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.

Keywords: oxastannetane, tin-Peterson reaction, pentacoordinate stannate, homo-Brook type rearrangement, bis(β-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(β-hydroxyalkyl)stannane.



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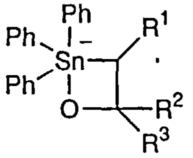
2: X = Si$^-$



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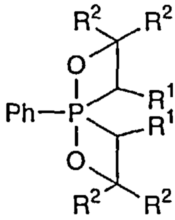

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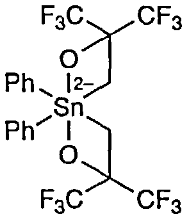

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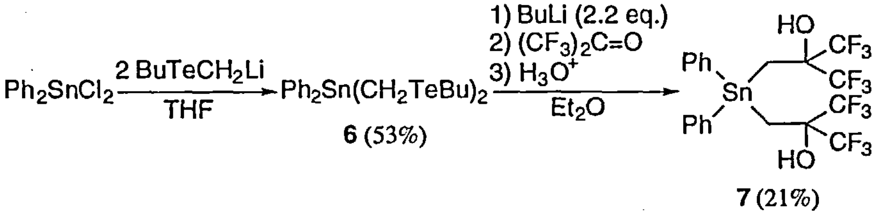
RESULTS AND DISCUSSION

Synthesis of bis(β-hydroxyalkyl)stannane

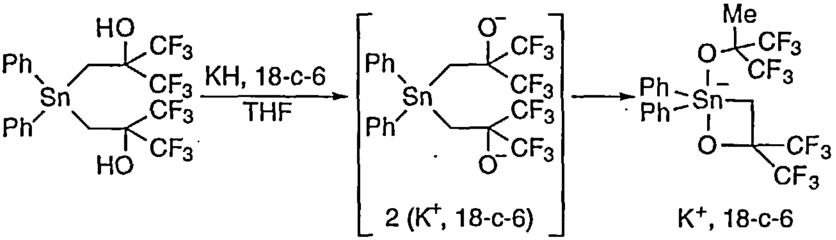
Bis(β-hydroxyalkyl)stannane **7** as a key intermediate was synthesized as shown in Scheme 1. Bis(butyltelluromethyl)stannane **6** was prepared in 53% yield by the reaction of dichlorodiphenylstannane with 2 equiv. of butyltelluromethyllithium in THF, which was generated *in situ* by treatment of bis(butyltelluro)methane with *n*-BuLi according to the literature[6]. The reaction of bis(lithiomethyl)stannane[7], which was generated by the treatment of **6** with 2.2 equiv. of *n*-BuLi, with hexafluoroacetone, followed by aq. NH_4Cl gave bis(β-hydroxyalkyl)stannane **7** in 21% yield.



Scheme 1

Reaction of bis(β-hydroxyalkyl)stannane with potassium hydride

The reaction of **7** with potassium hydride in THF in the presence of 18-crown-6 was monitored by ^{19}F and ^{119}Sn NMR spectroscopy at room temperature. Just after the addition of potassium hydride, the reaction mixture showed a signal at δ_{Sn} –148.4 in ^{119}Sn 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[1,2-oxastannetanide] **5**. The ^{119}Sn chemical shift of **9** is δ_{Sn} –246.4, which is a reasonable value as the pentacoordinate tin compound[4]. ^1H, ^{13}C and ^{19}F NMR data also supported this structure.



7 (δ_{Sn}–103.2) **8** (δ_{Sn}–148.4) **9** (δ_{Sn}–246.4)

Scheme 2

This compound is considered to be formed by novel tin-1,3-migration 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.

Acknowledgments

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