Regio- and Diastereoselective Aldol Reaction Using Cyclic Germyl or Stannyl Dienolates

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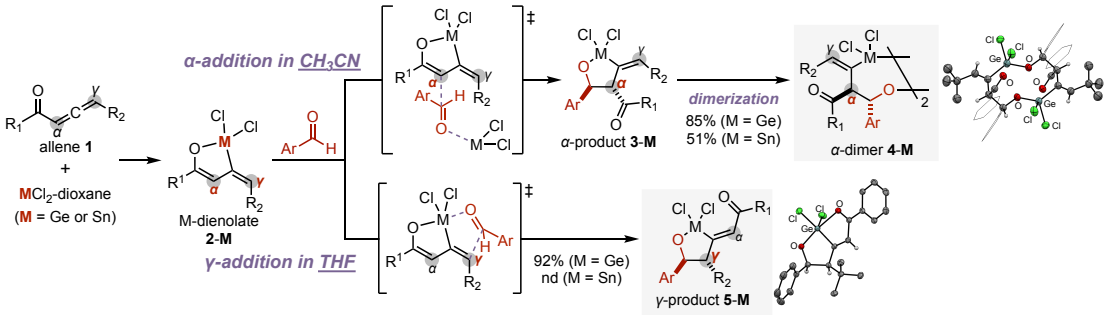
Dienolates, conjugated enolates, possess two nucleophilic carbons. The regioselectivity of the nucleophilic attack of a dienolate with an electrophile (E^+) generally depends on the characters of metal center of the dienolate; *Li*-dienolate preferentially reacts at the α-position, while *Si*-dienolate reacts at the γ-position.[1] However, the interrelationship between the nature of metal center and the regioselectivity remains elusive.[2] Herein, we focus on the group 14 metal-dienolates, particularly *Ge*- and *Sn*-dienolates.[3]

Cyclic *Ge*- and *Sn*-dienolates **2-M** were prepared from allenylketone **1** and MCl_2-dioxane (M = Ge or Sn). The nucleophilic addition of generated *Ge*-dienolate **2-Ge** with aldehydes in CH_3CN proceeds predominantly at the α-position, followed by subsequent dimerization of the α-product **3-Ge** to afford the α-dimer **4-Ge** with perfect regio- and diastereoselectivity. Conversely, in THF, the reaction occurs exclusively at the γ-position to yield the γ-product **5-Ge** selectively. Mechanistic investigations unveiled that the solubility of α-dimer **4-Ge** and the loading amount of the $GeCl_2$-dioxane are important to control the regioselectivity of the Ge-dienolate **2-Ge**. In stark contrast, *Sn*-dienolate **2-Sn** consistently undergoes α-addition to form the α-dimer **4-Sn**, irrespective of the solvent conditions. These findings exhibit that only the *Ge*-dienolate **2-Ge** can switch the reacting position depending on the reaction conditions. This fact is not shared by *Si*-dienolate, which exclusively forms γ-product, and *Sn*-dienolate **2-Sn**, which selectively yields α-dimer **4-Sn**.



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