

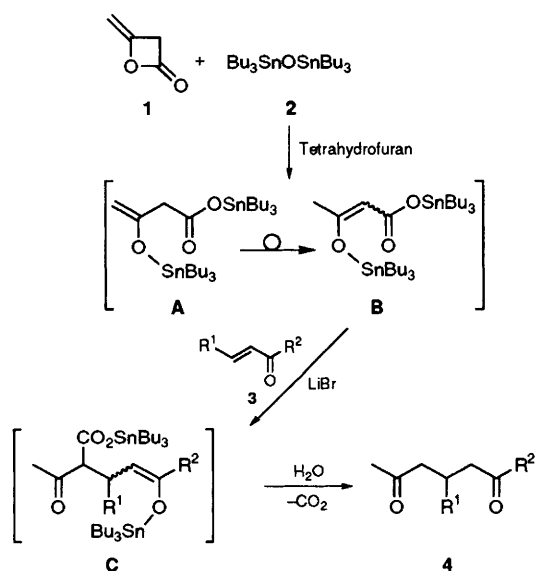
Novel Method for Generation of an Organotin Enolate by the Cleavage of Diketene with Bis(tributyltin) Oxide, and its Michael Reactions

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Generation of a novel type of organotin enolate has been accomplished by the regioselective ring cleavage of diketene with bis(tributyltin) oxide; the enolate afforded the first example of Michael addition in reactions using organotin(IV) enolates.

Organotin alkoxides are known to promote ring cleavage of β -lactones,¹ regioselectively at the acyl-oxygen bond. Diketene **1** has a highly reactive β -lactone ring, and is a versatile compound from which a large number of commercial products are prepared.² We have recently reported the tri-n-butyltin methoxide (Bu_3SnOMe) promoted ring cleavage of diketene;³ a tin enolate intermediate was formed,



which reacted with alkyl halides to give acetyl acetoacetate derivatives. Although it should be possible to obtain various organotin enolates from diketene, there have been few reports of enolate formation by ring cleavage with organotin alkoxides. We have now found that a novel type of organotin enolate derived from the ring cleavage of diketene **1** with bis(tributyltin) oxide [$(\text{Bu}_3\text{Sn})_2\text{O}$] **2** participated effectively in Michael addition. In particular, this is the first example of Michael addition in reactions using organotin(IV) enolates.

Scheme 1 summarizes the present reaction. Initially, the reaction of **1** and $(\text{Bu}_3\text{Sn})_2\text{O}$ **2** was carried out at 0°C . The IR band due to **1** at 1850 cm^{-1} disappeared after 10 min; regioselective ring cleavage of **1** takes place at the acyl-oxygen bond to afford the tin enolate **A**, which isomerizes to the more stable enolate **B**. The $^1\text{H NMR}$ signal of the vinyl proton of **B** was a singlet at δ 4.80. The Michael reaction of **B** with **3** was carried out at 40°C for 5 h. The mixture was quenched with aqueous MeOH and column chromatography (hexane-EtOAc, 10:1) gave the diketone **4**. We assume that the adduct **C** was formed, but it could not be isolated because decarboxylation occurred during work up. No side reaction, e.g. 1,2-addition, occurred.

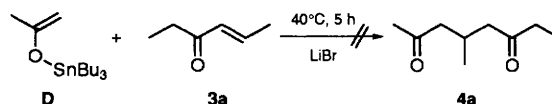
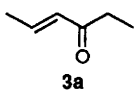
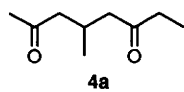
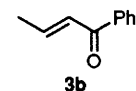
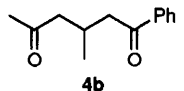

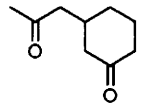
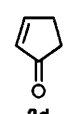
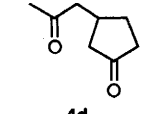
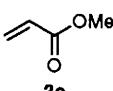
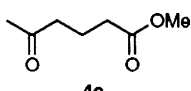


Table 1 Michael addition with α,β -unsaturated ketones and enolate derived from **1**^a

Entry	Enone 3	1,5-Diketone 4	Yield (%)
1			74
2			68
3			70
4			40
5			65

^a Conditions: enolate **B** formation: diketene **1** (2 mmol), $(\text{Bu}_3\text{Sn})_2\text{O}$ **2** (2 mmol), 0 °C, 10 min; reaction with enone: enone **3** (2 mmol), LiBr (2 mmol), tetrahydrofuran (2 ml), 40 °C, 5 h.

Various 1,5 diketones **4** were prepared by this reaction (Table 1) including cyclic substrates (**4c** and **4d**) and the keto ester **4e**. The reaction with hex-2-en-3-one **3a** afforded 4-methyloctane-2,6-dione **4a** in 74% yield (entry 1). The use of LiBr as an additive increased the yield of the product **4**. In the absence of LiBr, **4a** was obtained in 51% yield, and the aromatic enone **3b** gave **4b** in 52% yield (entry 2).

Although tin(II) enolates are known to promote Michael addition,⁴ organotin(IV) enolates have not hitherto proved to be useful. In fact, under similar conditions, the reaction of **3a** with tin enolate **D**, which has no terminal functional groups, did not afford the desired product **4a** (Scheme 2). The tin enolate **B** thus exhibits unusual reactivity. The terminal carbostannyloxy group of **B** is essential for Michael addition. Presumably, the electron withdrawing properties of, or intramolecular coordination involving, the carbostannyloxy group, would affect the nucleophilicity of the tin enolate.

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