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# Preparation of α,β-Unsaturated Methyl Ketones from Diketene Using Bis(tributyltin) Oxide

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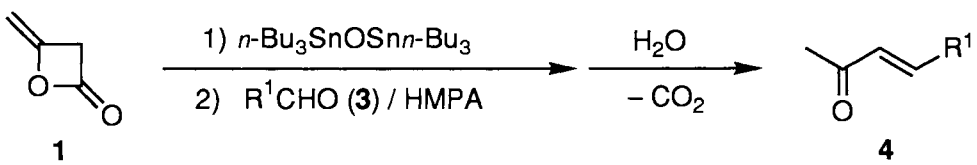
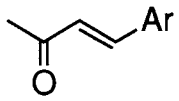
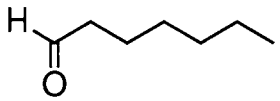
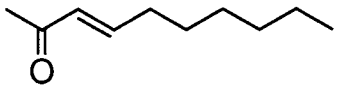
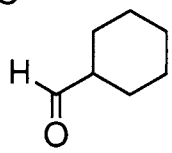
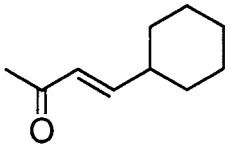
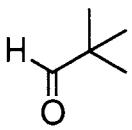
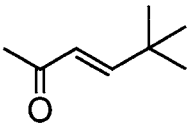
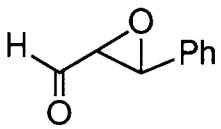
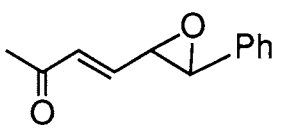
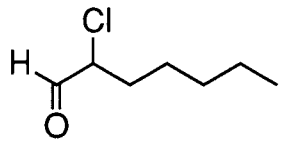
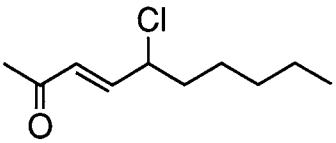
Novel type tin enolate is easily formed by the regioselective ring cleavage of diketene with Bis(tributyltin) oxide [$(n\text{-Bu}_3\text{Sn})_2\text{O}$]. The enolate caused carbon-carbon bond formation with aldehydes. As a result, α,β-unsaturated methyl ketones were obtained in good yields, accompanied by decarboxylation.

Organotin alkoxides are known to promote ring cleavage of β-lactone.[1] The cleavage takes place at the acyl-oxygen bond regioselectively. 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] Although various organotin enolates would be available by the ring cleavage of diketene, their formation is hardly reported by using organotin alkoxides.[3] We have recently reported tributyltin methoxide ($n\text{-Bu}_3\text{SnOMe}$) promoted ring cleavage of diketene.[4] In this reaction, tin enolate intermediate was formed, which reacted with electrophiles to give various acetyl acetoacetate derivatives effectively. Here we found a novel method for generation of an organotin enolate by the ring cleavage of diketene (**1**) with bis(tributyltin) oxide [$(n\text{-Bu}_3\text{Sn})_2\text{O}$] (**2**).[5] Subsequent reaction with aldehydes (**3**) gave α,β-unsaturated ketones (**4**) (Eq. 1). By using the present method, various types **4** were obtained in good yields.




**1** **4** (1)

Table 1. Reaction of Diketene (**1**) with Aldehyde (**3**) Promoted by $(n\text{-}Bu_3Sn)_2O$ (**2**)[a)]

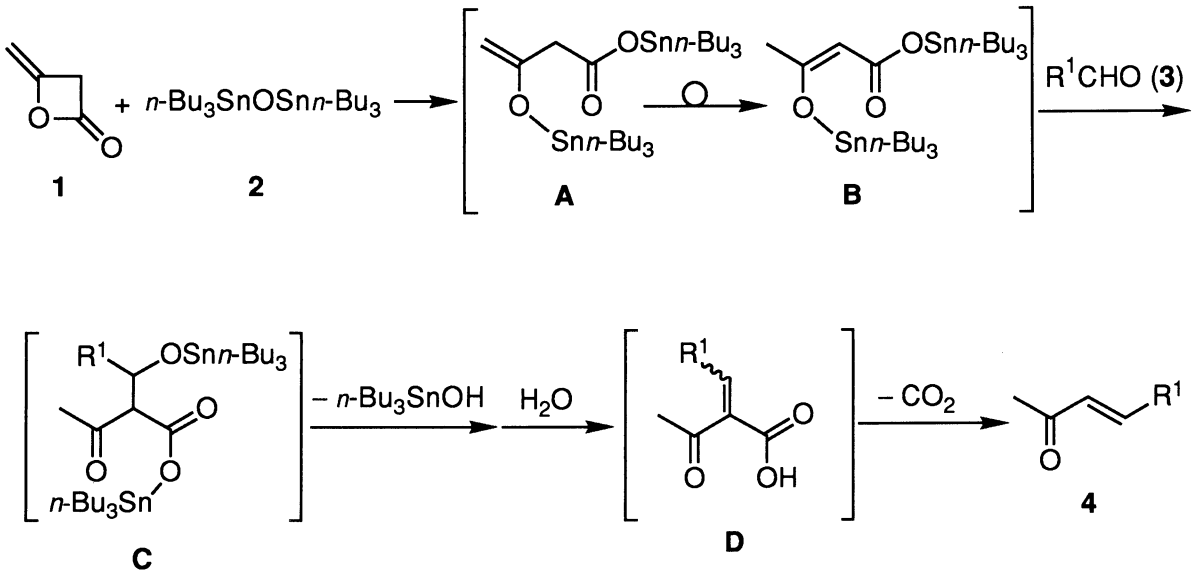
| Entry | RCHO (**3**) | | | Product (**4**) | | | Yield / % |
|---|---|---|---|---|---|---|---|
| 1 | ArCHO | Ar= Ph | **3a** |  | Ar= Ph | **4a** | 62 |
| 2 | | $p$-$NO_2C_6H_4$ | **3b** | | $p$-$NO_2C_6H_4$ | **4b** | 65 |
| 3 | | $p$-$ClC_6H_4$ | **3c** | | $p$-$ClC_6H_4$ | **4c** | 80 |
| 4 | | $p$-$CH_3C_6H_4$ | **3d** | | $p$-$CH_3C_6H_4$ | **4d** | 75 |
| 5 |  | | **3e** |  | | **4e** | 74 |
| 6 |  | | **3f** |  | | **4f** | 73 |
| 7 |  | | **3g** |  | | **4g** | 71 |
| 8 |  | | **3h** |  | | **4h** | 77 |
| 9 |  | | **3i** |  | | **4i** | 48 |

a)Reaction conditions; Step of **B** formation: Diketene (**1**) 2 mmol, $(n\text{-}Bu_2Sn)_2O$ (**2**) 2 mmol, THF 2 mL, 0 °C, 10 min. Step of reaction with aldehyde: RCHO (**3**) 2 mmol, HMPA 2 mmol, 40 °C, 4 h.

The following procedure is representative. Under nitrogen, **1** (2 mmol) was added to a tetrahydrofuran (2 mL) solution of **2** (2 mmol). The mixture was stirred at 0 °C for 10 min. IR absorption band around 1900 $cm^{-1}$ due to **1** disappeared, which indicated the ring cleavage. Next, aldehyde (**3**) (2 mmol) and hexamethylphosphoric triamide (HMPA) (2 mmol)[6)] were added, and the mixture was stirred at 40 °C for 4 h. After quenching with aq. MeOH (5 mL), the solvent was removed under reduced pressure. The residue was subjected to column chromatography eluting with 1:1 hexane/ethyl acetate. During work up, decarboxylation occurred, and product **4** was obtained.

Table 1 summarizes these results. For example, in the reaction with PhCHO (**3a**), benzalacetone (**4a**) was obtained in 62% yield (entry 1). Similarly, aldehydes, **3b-3d**, afforded the corresponding aromatic unsaturated ketones, **4b-4d**, in good yields (entries 2-4). The reaction also proceeded effectively in the case of aliphatic aldehydes **3e** to yield **4e** (entry 5). Aldehydes bearing bulky subsutituents, **3f** and **3g**, were also reactive to give **4f** and **4g** (entries 6 and 7). One of advantages of this reaction is that products were obtained under mild and neutral conditions. Hence, chemoselective reactions occurred in the case of bifunctional substrates. With α,β-epoxyaldehyde **3h**, vinylepoxide **4h** was obtained in 77% yield (entry 8). The reaction of α-chloroaldehyde **3i** gave γ-chloro-α,β-unsaturated ketone **4i** (entry 9), where reactive chloro group was not affected at all.[7)]

These reactions are explained as shown in Scheme 1. Initially, the ring cleavage of **1** occurs at the acyl-oxygen bond. As a result, tin enolate **A** is formed, which isomerizes to the stable one **B**.[8)] Next, **B** causes carbon-carbon bond formation with **3** to give **C**. The isolation of this aldol intermediate **C** was not successful, because decarboxylation occurred during work up. Presumably, **C** affords **D** which causes subsequent decarboxylation. As a result, α,β-unsaturated ketones **4** are obtained effectively.




Scheme 1.

Generally, organotin enolates gives aldol compounds by the reaction with aldehydes.[9)] In contrast, the present method provided direct formation of α,β-unsaturated ketones. No aldol products were obtained.

In summary, tin enolate **B** derived from the ring cleavage of diketene (**1**) with $(n\text{-Bu}_3\text{Sn})_2\text{O}$ (**2**) employed as an effective agent for the preparation of α,β-unsaturated ketones **4** by the reaction with aldehydes **3**. This method would enlarge not only the utility of diketene but also that of organotin chemistry.

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References

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2) R. J. Clemens, *Chem. Rev.*, **86**, 241 (1986).

3) Ishii et al. reported the ring cleavage of diketene with an organotin imine. H. Suzuki, I. Matsuda, K. Itoh, and Y. Ishii, *Bull. Chem. Soc. Jpn.*, **47**, 2736 (1974).

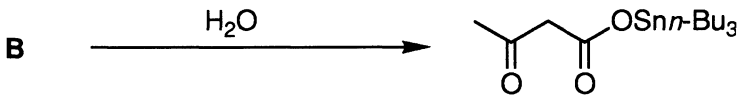
4) I. Shibata, N. Sumitomo, A. Baba, and H. Matsuda, *Chem. Express.*, **7**, 49 (1992).

5) For generation of organotin(IV) enolates, transmetalation of lithium enolate, [5a] hydrostannation of α,β-unsaturated ketones, [5b] and transesterification of enol acetates,[5c] are known as general procedures.
a) Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, **1981**, 162;
b) M. Pereyre and J. Valade, *Bull. Soc. Chem. Fr.*, **1967**, 1928; c) M. Pereyre, B. Bellegarde, J. Mendelsohn, and J. Valade, *J. Organomet. Chem.*, **11**, 97 (1968).

6) Activation of organotin enolates by HMPA has been reported. A. Baba, M. Yasuda, K. Yano, I. Shibata, and H. Matsuda, *J. Chem. Soc., Perkin Trans 1*, **1990**, 3205.

7) For example, the spectral data of newly produced compound **4i** are as follows: IR (neat): 1630, 1680 cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 0.90 (t, 3H, *J*=6.8 Hz, $CH_3$), 1.26-1.89 (m, 8H, $CH_2$), 2.29 (s, 3H, $CH_3C$=O), 4.45 (q, 1H, *J*=7.3 Hz, CHCl), 6.22 (d, 1H, *J*=15.6 Hz, COCH=C), 6.70 (dd, 1H, *J*=7.3 and 15.6 Hz, CH=C); $^{13}$C NMR ($CDCl_3$): δ 13.91, 22.39, 25.89, 27.51, 31.11, 37.68, 60.27, 130.67, 144.93, 197.98.

8) In the reaction using $Bu_3SnOMe$, similar rearrangement to the stable type enolate took place.[4] $^1$H NMR spectra indicated the vinyl proton of **B** as a singlet signal at 4.80 ppm. Moreover, hydrolysis of **B** afforded stannyl ester.




9) M. Pereyre, P. J. Quintard, and A. Rahm, "Tin in Organic Synthesis," Butterworth, London (1987), p. 286.

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