

Communications to the Editor

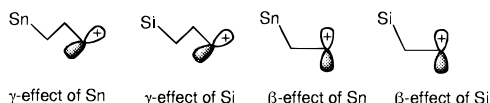
Remarkable γ -Effect of Tin: Acid-Promoted Cyclopropanation Reactions of α -((Alkoxy carbonyl)oxy)stannanes with Alkenes

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Recently the importance of the γ -effect of tin, the ability of tin to stabilize an electron-deficient center at the γ -position, has been recognized not only from mechanistic aspects¹ but also from synthetic view points.² The magnitude of the γ -effect of tin has been studied extensively mainly in solvolytic reactions,^{1c} and it is compared with the γ -effect of silicon and the β -effects of silicon³ and tin.⁴ However, it is rather difficult to evaluate the γ -effect of tin when we consider its synthetic applications. Since we have been interested in synthetic applications of the γ -effect of tin, we devised a system where intramolecular competition between γ -elimination of tin and β -elimination of tin or silicon can be examined. We report herein the preliminary results of this study and its applications to novel tin carbenoids⁵ which undergo inter- and intramolecular cyclopropanation reactions with olefins.



In order to generate a carbocation having both γ -tin and β -tin or silicon, we carried out the addition of α -tin-substituted carbocations to allyltin and -silicon compounds. Thus, the aryl-((alkoxy carbonyl)oxy)methylstannane **1**⁶ was treated with

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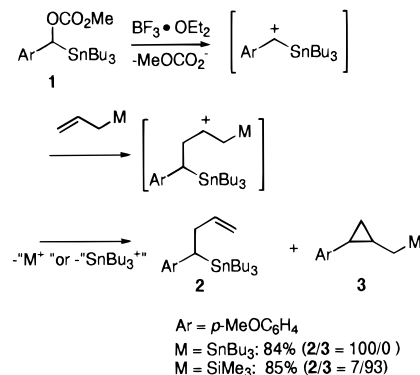
(2) Generation of a carbocation γ to tin usually leads to cyclopropanation if there is no conformational restrictions. See: (a) Pereyre, M.; Quintard, J-B.; Rahm, A. *Tin in Organic Synthesis*; Butterworth & Co.: London, 1987; p 235. (b) Davis, D. D.; Chambers, R. L.; Johnson, H. T. *J. Organomet. Chem.* **1970**, *25*, C13. (c) Peterson, D. J.; Robbins, M. D. *Tetrahedron Lett.* **1972**, *13*, 2135. (d) Teratake, S.; Morikawa, S. *Chem. Lett.* **1975**, 1333. (e) Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704. (f) Ueno, Y.; Ohta, M.; Okawara, M. *Tetrahedron Lett.* **1982**, *23*, 2577. (g) Murayama, E.; Kikuchi, T.; Sasaki, K.; Sootome, N.; Sato, T. *Chem. Lett.* **1984**, 1897. (h) Johnson, C. R.; Kadow, J. F. *J. Org. Chem.* **1987**, *52*, 1493. (i) Sato, T. *Synthesis* **1990**, 259. (j) Plamondon, L.; Wuest, J. D. *J. Org. Chem.* **1991**, *56*, 2066. (k) Sato, T.; Nagatsuka, S. *Synlett* **1995**, 653. (l) Beddoes, R. L.; Lewis, M. L.; Quayle, P.; Johal, S. *Tetrahedron Lett.* **1995**, *36*, 471. (m) Isono, N.; Mori, M. *J. Org. Chem.* **1996**, *61*, 7867.

(3) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677 and references cited therein. The γ -elimination of silicon to form a cyclopropane ring has been reported. See: Sakurai, H.; Imai, T.; Hosomi, A. *Tetrahedron Lett.* **1977**, *46*, 4045.

(4) Lambert, J. B.; Wang, G.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422 and references cited therein.

(5) (a) Clark, H. C.; Willis, C. J. *J. Am. Chem. Soc.* **1960**, *82*, 1888. (b) Seyferth, D.; Dertouzos, H.; Suzuki, R.; Mui, J. Y. P. *J. Org. Chem.* **1967**, *32*, 2980. (c) Seyferth, D.; Armbricht, F. M.; Prokai, B.; Cross, R. J. *J. Organomet. Chem.* **1966**, *6*, 573. (d) Seyferth, D.; Armbricht, F. M. *J. Am. Chem. Soc.* **1969**, *91*, 2616. (e) Seyferth, D.; Lambert, R. L. *J. Organomet. Chem.* **1975**, *91*, 31.

Scheme 1



Scheme 2

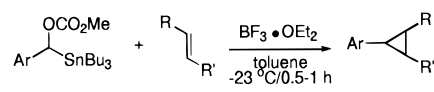


Table 1. Cyclopropanation Reactions of **1** with Olefins^a

Entry	Ar	Olefin	Product	Yield(%) ^d
1	<i>p</i> -MeOC ₆ H ₄			94
2				45
3				70
4				87
5				70 ^f
6	Ph			50
7				87

^a Reaction condition: 0.20 mmol of **1**, 1.1 equiv of olefin, 1.1 equiv of BF₃·OEt₂ in toluene (0.50 mL) at -23 °C for 0.5–1 h. ^b *cis/trans* = >98/2 by ¹H NMR^g. ^c *cis/trans* = 89/11. ^d Isolated yield *via* flash chromatography. ^e 2.0 equiv of olefin was used. ^f 19% (based on **1**) of dicyclopentane compound was obtained.

BF₃·OEt₂ in the presence of allyltributylstannane or allyltrimethylsilane (Scheme 1). The reaction with allyltributylstannane gave rise to exclusive formation of the allylated product (**2**). The reaction with allyltrimethylsilane, however, afforded cyclopropane **3**⁷ together with a small amount of **2**. These results indicate that β -elimination of tin is faster than γ -elimination.

(6) α -Oxystannanes are widely utilized in organic synthesis. Anodic oxidation: (a) Yoshida, J.; Ishichi, Y.; Ise, S. *J. Am. Chem. Soc.* **1992**, *114*, 7594. (b) Yoshida, J.; Morita, Y.; Ishichi, Y.; Ise, S. *Tetrahedron Lett.* **1994**, *35*, 5247. Transmetalation to lithium: (c) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481. (d) Tomooka, K.; Igarashi, T.; Watanabe, M.; Nakai, T. *Tetrahedron Lett.* **1992**, *33*, 5795. Stille type cross coupling: (e) Ye, J.; Bhatt, R. K.; Falck, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 1.

(7) Cyclopropane **3** was obtained as a mixture of two isomers (*cis/trans* = 87/13).

Table 2. Intramolecular Cyclopropanation Reaction

entry	n	R ₂	R ₃	yield(%)
1	1	H	H	96
2	1	Me	Me	89
3	1	Me	Me ₂ C=CH(CH ₂) ₂	100
4	2	H	H	100
5	3	H	H	<5
6 ^a	3	H	H	16

^a BF₃·OEt₂ (1.1 equiv) was used instead of *p*-TsOH·H₂O.

tion of tin, whereas γ -elimination of tin is faster than β -elimination of silicon. Since β -elimination of silicon is known to be very fast and is utilized in various synthetic reactions,⁸ γ -elimination of tin is hoped to enjoy versatile synthetic applications.

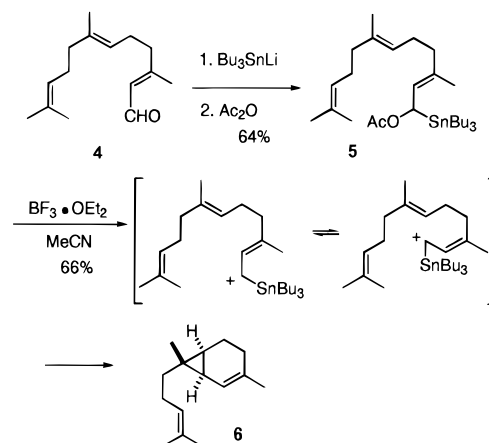
The success of the cyclopropanation reaction with the allylsilane prompted us to investigate the generality of this reaction. Thus, we examined the BF₃·OEt₂ promoted reaction of **1** in the presence of various olefins (Scheme 2). As summarized in Table 1, the present reaction is generally applicable to alkyl-substituted olefins and conjugated olefins such as styrene derivatives and 1,3-dienes. Although aryl-substituted α -((alkoxycarbonyl)oxy)stannanes served as good precursors for tin-substituted carbocations, the reactivities of alkyl-substituted analogues were low and the starting materials were recovered unchanged under similar conditions.

The intramolecular version of this reaction was also successful (Table 2). The cyclization to form six- and seven-membered rings took place smoothly, but the eight-membered ring product was obtained in low yield even with BF₃·OEt₂.

The synthetic utility of the present cyclopropanation reaction is demonstrated by the following very simple and straightforward synthesis of sesquicarenene (**6**).¹⁰ In this case the acetoxy group is a better leaving group than the (methoxycarbonyl)oxy

(8) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin Heidelberg, 1983; p 173.

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Scheme 3

group. Thus, the starting material for the cyclopropanation (**5**) was prepared by the addition of stannyl lithium to the readily available aldehyde **4**,¹¹ followed by the reaction with acetic anhydride (Scheme 3). The treatment of **5** with BF₃·OEt₂ in CH₃CN gave the cyclized product **6** in 66% yield. Presumably, pre-equilibration of the *E/Z* isomers¹² of the allyl cation intermediate takes place as shown in Scheme 3.

In summary, the γ -elimination of tin was proved to be faster than the β -elimination of silicon, although it is slower than the β -elimination of tin. Using the facile γ -elimination of tin, inter- and intramolecular cyclopropanation reactions of α -((alkoxycarbonyl)oxy)stannanes with olefins have been developed. Further mechanistic investigations and studies concerning synthetic applications are underway.

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Supporting Information Available: A typical experimental procedure and listing of spectral data (8 pages). See any current masthead page for ordering and Internet access instruction.

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(11) Dodd, D. S.; Oehlschlager, A. C. *J. Org. Chem.* **1992**, *57*, 2794.

(12) Marshall, J. A.; Jablonowski, J. A.; Elliott, L. M. *J. Org. Chem.* **1995**, *60*, 2662.